

EXHIBIT 6

UNITED STATES DISTRICT COURT
DISTRICT OF DELAWARE

BRIDGESTONE SPORTS CO., LTD., and
BRIDGESTONE GOLF, INC.,

Plaintiffs,

v.

ACUSHNET COMPANY,

Defendant.

Case No. 05-CA-132 (JJF)

**INVALIDITY EXPERT REPORT OF DR.
JACK KOENIG**

ACUSHNET COMPANY,

Counterclaimant,

v.

BRIDGESTONE SPORTS CO., LTD., and
BRIDGESTONE GOLF, INC.,

Counterdefendant.

77. I have reviewed the Nesbitt '940 patent in light of claims 1 and Nesbitt '940 discloses each and every limitation of claims 1 and 2, and therefore anticipates claims 1 and 2. A copy of the Nesbitt '940 prior art reference is attached to this report as Exhibit G.

i. Claim 1

78. The preamble to claim 1 of the '961 patent states that it relates to "a multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition comprising:"

79. Nesbitt '940 also relates to a multi-piece solid golf ball, with a solid core, an inner cover layer and an outer cover layer. (Ex. G, Nesbitt '940, at Abstract; col. 16, lines 49-57; col. 44, lines 60-65; Tables 30-37)

80. Claim 1 of the '961 patent requires a base rubber composition that comprises 20 to 100 wt % of a first polybutadiene ("polybutadiene (a)") having certain characteristics:

| '961 Claim Requirements for Polybutadiene (a) |
|--|
| Cis-1,4 content of at least 60% |
| 1,2 vinyl content of at most 2% |
| Viscosity η at 25 °C as a 5 wt % solution in toluene of up to 600 mPa·s |
| Synthesized using a rare-earth catalyst |
| Satisfying the relationship: $10B + 5 \leq A \leq 10B + 60$ A = Mooney viscosity B = Ratio Mw/Mn |

81. Viscosity is a measure of the resistance of a liquid or solution to flowing. A high viscosity means the fluid has a slow flow, i.e. like molasses. A low viscosity

means the liquid has a high flow, i.e. like water. With polymers, as the molecular weight increases, the viscosity usually increases.

82. Mooney viscosity is the measurement of viscosity used with rubbers. Since rubbers are solids, the Mooney viscosity measures the resistance of the rubbers to distortion.

83. Polydispersity (M_w/M_n) is a measure of the different lengths (and therefore weight) of the polymer molecules. M_w is the weight average molecular weight, which is the weight of molecules of a given length divided by the total weight. M_n is the number average molecular weight, which is the number of molecules of a given length divided by the total number of molecules. When the molecules are all of the same length, the polydispersity is one. The higher the polydispersity, the broader the differences in the lengths and weights of the molecules.

84. Nesbitt '940 discloses several core compositions that include polybutadiene rubbers that satisfy the requirements for the '961 patent's polybutadiene (a). One such example is Table 6 of the Nesbitt '940 patent, reproduced below, which includes Neo Cis 60 polybutadiene:

Most preferably, a core formulation in accordance with the present invention is as follows in Table 6.

TABLE 6

| Ingredients | Parts | Wt % |
|---------------------------|-------|-------|
| Cariflex 1220x (HC P 820) | 40 | 24.64 |
| Neo Cis 60 | 31 | 18.48 |
| Neo Cis 20 | 30 | 18.48 |
| Zinc Oxide | 24 | 14.78 |
| Tungsten powder | 0.17 | 0.105 |
| Zinc Stearate | 10.3 | 10.04 |
| Zinc Diacrylate (ZDA) | 20.5 | 12.63 |
| Red MB | 0.14 | 0.086 |

TABLE 6-continued

| Ingredients | Parts | Wt % |
|-----------------|-------|------|
| Trigenox 42 40R | 1.34 | 0.76 |
| Total | 162.4 | 100 |

85. Table 6 shows a core formulation that is made up of 100 parts of base rubber that consists of three different commercially available types of polybutadiene

rubber: (a) 40 parts of Cariflex 1220x, (b) 30 parts of Neo Cis 60 and (c) 30 parts of Neo Cis 40. The remaining ingredients in Table 6 are not part of the base rubber composition of the core formulation.

86. The weight percent (wt %) of the ingredients in Table 6 represents the amount of each ingredient as a percentage of the entire core formulation. Therefore, although Neo Cis 60 accounts for 18.48% of the entire core formulation, it accounts for 30% (30 parts out of 100) of the base rubber. Similarly, Cariflex 1220x accounts for 40% (40 parts out of 100) and Neo Cis 60 accounts for 30% (30 parts out of 100) of the base rubber described in Table 6. As explained in detail below, Neo Cis 60 satisfies all of the requirements for the polybutadiene (a) of the '961 patent.

87. Table 2 of the Nesbitt '940 patent, reproduced below, discloses the properties of Neo Cis 40 and Neo Cis 60, respectively. Table 2 discloses that the cis-1,4 content of Neo Cis 60 is 97.5% and that it has a 1,2 vinyl content of 0.8%.

| TABLE 2 | |
|---|-----------------|
| Properties of Neo Cis | |
| <u>Properties of Raw Polymer</u> | |
| Microstructure | |
| 1,4 cis (typical) | 97.5% |
| 1,4 trans (typical) | 1.7% |
| Vinyl (typical) | 0.8% |
| Volatile Matter (max) | 0.75% |
| Ash (max) | 0.30% |
| Stabilizer (typical) | 0.50% |
| Moonsey Viscosity, MI 1 + 4 at 120 °C | 30-40 and 60-80 |
| <u>Properties of compound (typical)</u> | |
| Vulcanization at 145° C. | |
| Tensile strength, 35 cure, | 15 MPa |
| Elongation, 35 cure, | 400% |
| 100% modulus, 35 cure, | 0.5 MPa |

88. Independent laboratory testing on Neo Cis 60 was performed at my request to determine the solution viscosity of the Neo Cis 60 rubber at 25°C, as a 5 wt % solution in toluene.

89. The viscosity test discussed in the '961 patent uses a standard solution according to Japanese Industrial Standard (JIS) Z8809. JIS Z8809, included as Exhibit H, references JIS Z8803 (attached as Exhibit I), which relates to methods of measuring viscosity of liquids.

90. Therefore, at my direction, Alan Sentman, Ph.D., of Polymer Solutions, Inc. of Blacksburg Virginia, conducted solution viscosity measurements of Neo Cis 60 in accordance with JIS Z8809 and JIS Z8803.

91. The solution viscosity was obtained by using the protocol set forth in the '961 patent by dissolving 2.28 grams of polybutadiene to be measured in 50 mL of toluene and carrying out the measurement with a viscometer at 25°C using a standard solution for the viscometer. The viscometer was calibrated prior to testing the rubber sample through the use of certified viscosity standards. (*See* Ex. J, Certificates of Viscometer Calibration).

92. I observed the laboratory and testing methods of Polymer Solutions and it is my expert opinion that the tests performed were done properly and objectively.

93. The solution viscosity of Neo Cis 60 is 435.30 mPa·s. (Ex. K, Viscosity Calculation Spreadsheet).

94. The samples of Neo Cis BR-60 and Neo Cis BR-40 were obtained from the manufacturer, Polimeri Europa of Milan, Italy, through its United States distributor, Alternative Rubber and Plastics, Inc., of Amherst, NY.

95. As noted in the Nesbitt '940 patent, Neo Cis BR-60 and BR-40 were previously manufactured by Enichem Elastomers. (Ex. G, Nesbitt '940, col. 7, lines 44-45). Polimeri Europa merged with Enichem in or around 2001 and has since continued to

manufacture and sell Enichem's elastomer products, including Neo Cis BR-60 and BR-40. (See Ex. M, Polimeri Europa Webpage for BR-40 and BR-60).

96. Polimeri Europa confirmed to me in a telephone conversation and further by email to Acushnet attorneys that the Neo Cis BR-60 and BR-40 rubbers it currently manufactures and provides for sale in the United States are the same as the Neo Cis BR-60 and Neo Cis BR-40 that were manufactured by Enichem. (Ex. N, email from Polimeri Europa). I also confirmed this fact in a telephone conversation with Alternative Rubber and Plastics.

97. In fact, when shipping Neo Cis BR-60 and BR-40, Polimeri Europa currently includes the Material Safety Data Sheet for these rubbers that was created and used by Enichem. (Ex. O, MSDS Sheet)².

98. Moreover, in my experience, a manufacturer will not change the formulation of a commercially available rubber without changing the name of the rubber.

99. Neo Cis 60 is synthesized using neodymium, which is a rare-earth catalyst. (Ex. G, Nesbitt '940, at col. 14, lines 9-13.)

100. Table 2 of the Nesbitt '940 patent states that the Mooney viscosity of Neo Cis 60 is 60 to 66. (Ex. G, Nesbitt '940, at Table 2) The Nominal Mooney viscosity of Neo Cis 60 is 63. (Exhibit M, Polimeri Europa Product Webpage).

² To independently confirm that the Neo Cis samples from Polimeri Europa were the same as the Neo Cis rubber manufactured by Enichem, I requested Polymer Solutions, Inc., of Blacksburg, Virginia to run NMR tests on the samples to determine their 1,2-vinyl content. The results show that Neo Cis BR-60 had a 1,2 vinyl content of 0.83% and Neo Cis BR-40 had a 1,2 vinyl content of 0.82 %. (Exhibit P, NMR Results). These values are consistent with the values published in the Nesbitt '940 patent, at Table 2, which indicate the rubbers have a 1,2 vinyl content of 0.8 %.

101. At my direction, independent laboratory testing by Polymer Solutions, Inc. was performed on Neo Cis 60 to confirm the ratio of its weight average molecular weight Mw to its number average molecular weight Mn.

102. I observed the laboratory and testing methods of Polymer Solutions and it is my expert opinion that the tests performed were done properly and objectively.

103. The ratio of Neo Cis 60's weight average molecular weight Mw to its number average molecular weight Mn is 2.919. (Exhibit Q).

104. Based on its Mooney Viscosity ($A=63$) and the Mw/Mn Ratio ($B=2.919$), Neo Cis 60 satisfies the required relationship: $10B + 5 \leq A \leq 10B + 60$, as shown below:
 $10(2.919) + 5 \leq 63 \leq 10(2.919) + 60$; which equates to: $34.19 \leq 63 \leq 89.19$

105. In summary, Neo Cis 60 has all of the properties that are required for the polybutadiene (a) disclosed in claim 1 of the '961 patent:

| '961 Claim Requirements for Polybutadiene (a) | Neo Cis 60 |
|---|---|
| Cis-1,4 content of $\geq 60\%$ | 97.5% |
| 1,2 vinyl content $< 2\%$ | 0.8% |
| Solution viscosity ≤ 600 mPa·s | 435.30 mPa·s |
| Satisfying the relationship $10B + 5 \leq A \leq 10B + 60$ A = Mooney Viscosity B = Polydispersity | Mooney = 63 Polydispersity = 2.919 $34.19 \leq 63 \leq 89.19$ Equation is satisfied. |
| Rare Earth Catalyst | Neodymium |

106. Claim 1 further requires 0 to 80 wt % of a second diene rubber ("diene rubber (b)"). Referring back to Table 6 of the Nesbitt '940 patent, it discloses a core

113. R1 connotes the presence of carbon, making the molecule organic, while S connotes the presence of sulfur, making the molecule an organic sulfur compound.

114. The Nesbitt '940 patent states that such compounds can be added to the core formulation in the amounts indicated in the incorporated patents. The Sullivan '884 patent discloses that dithiocarbamates can be included in amounts between 0.1 to 0.5 parts by weight. This is entirely within the claimed range for organosulfur compounds in the '961 patent. (Ex. R).

115. Claim 1 further requires 5 to 80 parts by weight of an inorganic filler.

116. Zinc oxide is an inorganic filler. (Ex. G, Nesbitt '940, at col. 12, lines 56-65).

117. Table 6 of the Nesbitt '940 patent discloses a core formulation with 24 parts by weight of zinc oxide, and inorganic filler, which is within the 5 to 80 parts by weight required by the '961 patent.

118. Claim 1 further requires 0.1 to 5 parts by weight of an organic peroxide.

119. Triganox 42-40B is an organic peroxide (Ex. G, Nesbitt '940, at col. 12, lines 8-24).

120. Table 6 of the Nesbitt '940 patent discloses a core formulation with 1.24 parts by weight of Triganox 42-40B, an organic peroxide, which is within the 0.1 to 5 parts by weight required by the '961 patent. In summary:

| '961 Claim Requirements Core Formulation | Table 6 Nesbitt '940 Prior Art Core Formulation |
|--|---|
| 20-100 wt % polybutadiene (a) | 30 wt % Neo Cis 60 |
| 0-80 wt % diene rubber (b) | 30 wt % Neo Cis 40 |
| 10 to 60 parts by weight unsaturated carboxylic acid | 20.5 parts Zinc Diacrylate |

| |
|---|
| Mooney viscosity of not more than 55 |
| Satisfying the relationship: $\eta \leq 20A - 550$ |
| A = Mooney viscosity η = solution viscosity of second polybutadiene |

128. In addition to disclosing a core formulation with 30 % Neo Cis 60, Table 6 of the Nesbitt '940 patent, referred to above, discloses a core formulation, which includes 30 parts Neo Cis 40, which is a second polybutadiene in the core formulation that is 100% polybutadiene, as required by claim 2 of the '961 patent. As explained in detail below, Neo Cis 40 satisfies all of the requirements for the second polybutadiene (b) disclosed in claim 2 of the '961 patent.

129. Table 2 of the Nesbitt '940 patent, reproduced above, discloses that the cis-1,4 content of Neo Cis 40 is 97.5% and that it has a 1,2 vinyl content of 0.8%.

130. Table 2 of the Nesbitt '940 patent discloses that the Mooney viscosity of Neo Cis 40 is 38 to 48. (Ex. G, Nesbitt '940, at Table 2) The Nominal Mooney viscosity of Neo Cis 40 is 43. (See Ex. M, Polimeri Europa Product Webpage).

131. Independent laboratory testing on Neo Cis 40 was performed at my request to determine the solution viscosity η of the Neo Cis 40 rubber at 25°C, as a 5 wt % solution in toluene.

132. The same protocol used to obtain the solution viscosity for Neo Cis 60 was used to obtain the solution viscosity of Neo Cis 40.

133. In my opinion, the tests performed were done properly and objectively.

134. The solution viscosity of Neo Cis 40 is 265.30 mPa·s. (Exhibit K).⁴

⁴ I understand that U.S. Patent No. 5,708,081 (Ex. S), filed in 1994, discloses that the solution viscosity for Neo Cis BR-40 as a 5 wt % solution in *styrene* is 330 mPa·s. The '961 patent requires the solution viscosity be measured in *toluene*. At my request, Polymer Solutions, Inc. further tested the solution

135. Based on its Mooney Viscosity ($A = 43$) and its Solution Viscosity ($\eta = 265.30$ mPa·s), Neo Cis 40 satisfies the required relationship: $\eta \leq 20A - 550$, as shown below:

$$265.30 \leq 20(43) - 550; \text{ which equates to: } 265.30 \leq 310$$

136. In summary, Neo Cis 40 has all of the properties that are required for the second polybutadiene (b) disclosed in claim 2 of the '961 patent:

| '961 Claim Requirements Second Polybutadiene (b) | Neo Cis 40 |
|--|---|
| Cis-1,4 content of $\geq 60\%$ | 97.5% |
| 1,2 vinyl content $\leq 5\%$ | 0.8% |
| Mooney Viscosity ≤ 55 | 43 |
| Satisfying the relationship $\eta \leq 20A - 550$ A = Mooney Viscosity η = Solution Viscosity | Mooney Viscosity = 43 Solution Viscosity = 265.30 mPa·s $265.30 \leq 310$ Equation is satisfied. |

137. It is my opinion that Table 6 of the Nesbitt '940 patent anticipates the core formulation disclosed in claim 1 and 2 of the '961 patent. It is my further opinion that Tables 34 and 37 of the Nesbitt '940 patent anticipate the Shore D hardness requirements for the covers disclosed in claims 1 and 2 of the '961 patent. Because claims 1 and 2 of the '961 patent were fully disclosed in the Nesbitt '940 prior art reference, it is my opinion that those claims are invalid.

138. It is my understanding that because claim 1 of the '961 patent uses the term "comprising" in describing the core formulation of the invention, additional materials may be present in the core formulation besides those specifically identified in

viscosity of the Neo Cis BR-40 sample as a 5 wt % solution in styrene and found the solution viscosity to be 336 mPa·s. (Ex. T, Styrene Solution Viscosity Calculation). This further confirms that the Neo Cis manufactured by Enichem has not changed.

include commercial success, a long-felt but unresolved need, failure of others, licensing, copying, and teaching away/skepticism of others.

159. It is my opinion that to the extent any element of claim 2 of the '961 patent is not fully described in the Nesbitt '940 patent, the '961 patent is still invalid based on obviousness.

1. Combination of Prior Art References

160. Claim 2 of the '961 patent is obvious by the combination of any of: (a) Nesbitt '940 patent; (b) U.S. Patent No. 6,486,261 ("Wu '261"); (c) the knowledge of those of ordinary skill in the art.

i. Nesbitt '940 in Combination with the Knowledge of One of Ordinary Skill in the Art

161. The Nesbitt '940 patent is discussed fully above.

162. A person of ordinary skill in the art, possessed with the understandings and knowledge reflected in the prior art, including the Nesbitt '940 patent, and motivated by the general problem facing the inventors, would have been led to make the combinations recited in claim 2 of the '961 patent.

163. Nesbitt '940 discloses golf ball core formulations made of blends of polybutadiene rubbers synthesized from neodymium catalysts (such as Neo Cis 40, Neo Cis 60, CB-22, CB-23 and CB-24), and from ultra high Mooney rubbers (such as BR-1220x). Nesbitt '940 further discloses such core compositions can also contain other polybutadiene rubbers with lower Mooney viscosities (such as BR-1220, Taktene 220 and Neo Cis 40) (*See* Ex. G, Nesbitt '940, at col. 6 line 55 – col. 9 line 56 and Table 6). It was known in the prior art that such polybutadiene rubbers were well-suited for the manufacture of golf ball cores.

164. I have reviewed the physical characteristics of the rubbers disclosed in Nesbitt '940 and have found that at least Neo Cis 40, Neo Cis 60 and CB-23 inherently possess the claimed attributes of polybutadiene (a) of claim 1 of the '961 patent.⁵

165. I have further found, as shown above, that at least Neo Cis 40 and BR-1220 inherently possess the claimed attributes of polybutadiene (b) of claim 2 of the '961 patent.

166. Nesbitt '940 suggests blending rubbers with the attributes of polybutadiene (a) with rubbers with the attributes of polybutadiene (b). It would have been a matter of routine optimization for one of ordinary skill in the art to blend a golf ball core composition using amounts of each type of polybutadiene within the ranges claimed by the '961 patent.

167. In fact, the idea of blending rubber compositions together to form a core was well-known to skilled artisans. In addition to Nesbitt' 940, other prior art patents disclose the blending of such rubbers for a golf ball core, including U.S. Patent No. 5,508,350 to Cadorniga ("Cadorniga '350") (Ex. W), U.S. Patent No. 6,486,261 to Wu et al. ("Wu '261") (Ex. X) and U.S. Patent No. 4,683,257 to Kakiuchi et al. (Kakiuchi '257) (Ex. Y), which is assigned to Bridgestone.

168. Cadorniga '350 discloses a golf ball core formulation made of 50 parts CB-23 and 50 parts Neo Cis 40. (Ex. W, Cadorniga '350, col. 7, line 36-65). The table from Cadorniga '350, reproduced below, further shows a blended polybutadiene golf ball

⁵ My analysis of Neo Cis BR-60 as a polybutadiene (a) of the '961 patent was fully discussed above. Please see Exhibit V for my analysis of Neo Cis 40 and CB-23.

core formulation with inorganic filler (zinc oxide), unsaturated carboxylic acid (zinc diacrylate) and peroxide⁶ within the claimed ranges of the '961 patent:

| FORMULAS | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---------------------------|------|------|------|------|------|------|-------|-------|-------|-------|
| MATERIALS | PHR | PHR | PHR | PHR | PHR | PHR | PHR | PHR | PHR | PHR |
| NEO CIS 40 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| CB 23 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| BARYTES | — | — | — | — | — | — | — | — | — | — |
| ZNO | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 | 19.75 | 19.75 | 19.75 | 19.75 |
| ZDA | 26.5 | 26.5 | 26.5 | 26.5 | 26.5 | 26.5 | 27.5 | 27.5 | 27.5 | 27.5 |
| ZN PALMELATE ¹ | — | 4.68 | — | — | 2.34 | — | — | 4.85 | — | — |
| ZN PALMELATE ² | — | — | — | 4.68 | — | 2.34 | — | — | 4.85 | — |
| ZN STEARATE ¹ | 4.68 | — | — | — | 2.34 | — | 4.85 | — | — | — |
| ZN STEARATE ² | — | — | 4.68 | — | — | 2.34 | — | — | 4.85 | — |
| REGRIND | — | — | — | — | — | — | — | — | — | — |
| PEROXIDE | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| PHYSICAL PROPERTIES | | | | | | | | | | |

169. Kakiuchi '257 further demonstrates that blending polybutadienes for core formulations was well known in the golf ball art much earlier than the priority date of the '961 patent. (Ex. Y, Kakiuchi '257, col. 2, lines 42-51).

170. Therefore, to the extent Nesbitt '940 does not explicitly disclose a golf ball formulation with the blend of rubbers described in the '961 patent, it would have been obvious based on the disclosures in Nesbitt '940 and the knowledge of one of ordinary skill in the art to formulate such a blend.

171. It was further well known in the prior art that the addition of sulfur compounds, as a peptizing agent or radical scavenger, aided in the processability of synthetic rubbers such as high cis polybutadiene. Moreover, the prior art shows that it was even well known in the golf ball art, that the use of sulfur compounds was beneficial. (See, e.g., Ex. D, U.S. Patent No. 5,252,652 and Ex. FF, U.S. Patent No. 4,556,220). For example, Bridgestone's '652 patent, filed in 1990 (twelve years prior to the '961 patent) discloses the benefits of sulfur compounds in the manufacture of improved golf ball cores. (See Ex. D, '652 patent, Abstract).

⁶ Cadorniga '350 specifically discloses that the organic peroxide dicumyl peroxide may be used. (Ex. W, Cadorniga '350, at col. 3, lines 14-16).

172. Therefore, to the extent one were to conclude that Nesbitt '940 does not disclose using a sulfur compound in the formulation of golf ball cores, such use was well known in the prior art, and would have been obvious to one of ordinary skill in the art to include a sulfur compound.

173. As such, it is my conclusion that, in addition to being anticipated as stated above, claims 1 and 2 of the '961 patent are also obvious in light of the Nesbitt '940 patent and the knowledge of those of ordinary skill in the art.

ii. Wu '261 in Combination with the Knowledge of One of Ordinary Skill in the Art

174. U.S. Patent No. 6,486,261 to Wu et al. ("Wu '261") (Ex. X) issued November 26, 2002, based on an application filed November 27, 2000 as a continuation-in-part of earlier filed applications dating back to December 24, 1998. I understand that the November 2000 filing date makes the Wu '261 patent prior art to the '961 patent.

175. A person of ordinary skill in the art, possessed with the understandings and knowledge reflected in the prior art, including the Wu '261 patent, and motivated by the general problem facing the inventors, would have been led to make the combinations recited in claim 2 of the '961 patent.

176. Wu '261 describes several core and cover golf ball compositions that may be used to provide desirable resiliency characteristics without sacrificing performance characteristics. (Ex. X, Wu '261, col. 5, lines 25-30).

177. Table 1 of the Wu '261 patent, reproduced below, lists several polybutadienes that may be used to produce resilient golf ball cores, and includes the rubbers discussed above with respect to the Nesbitt '940 patent, including Neo Cis BR-60, Neo Cis BR-40, Cariflex BR-1220, CB-23 and CB-22:

Cannon-Fenske

| ID | PSI Sample ID | Viscometer | Viscometer Constant | | Viscometer Coefficient | |
|---------|---------------|------------|---------------------|-------|------------------------|--|
| | | | c_1 | c_2 | | |
| CB-23 | 2006-668-01 | F12 | 0.2293 | | -18.38 | |
| BR-40 | 2006-668-02 | F12 | 0.2293 | | -18.38 | |
| BR-60 | 2006-668-03 | P94 | 1.1038 | | 257.59 | |
| BR-1220 | 2006-668-04 | F12 | 0.2293 | | -18.38 | |

Constants Calculated from Viscosity Standards

| Cannon-Fenske Viscometer F12 | |
|------------------------------|--------|
| c_1 | c_2 |
| 0.2293 | -18.38 |

| Cannon-Fenske Viscometer P94 | |
|------------------------------|--------|
| c_1 | c_2 |
| 1.1038 | 257.59 |

| Cannon-Fenske | | | | | | | | | | | | | |
|---------------|---------------|------------------------------|--------|--------|--------|--------|--------|----------------------|--------|---------|---------|--------|--|
| | | Flow Times (minutes,seconds) | | | | | | Flow Times (seconds) | | | | | |
| | | 1 | | 2 | | 3 | | 1 | 2 | 3 | Average | St Dev | |
| ID | PSI Sample ID | minute | second | minute | second | minute | second | | | | | | Kinematic Viscosity (mm ² /s) |
| CB-23 | 2006-668-01 | 15 | 7.71 | 15 | 7.06 | 15 | 6.37 | 907.71 | 907.06 | 906.37 | 907.05 | 0.67 | 208.02 |
| BR-40 | 2006-668-02 | 22 | 10.37 | 22 | 9.6 | 22 | 9.66 | 1330.37 | 1329.6 | 1329.66 | 1329.88 | 0.43 | 304.97 |
| BR-60 | 2006-668-03 | 7 | 36.06 | 7 | 36.03 | 7 | 35.81 | 456.06 | 456.03 | 455.81 | 455.97 | 0.14 | 502.72 |
| BR-1220 | 2006-668-04 | 4 | 32.12 | 4 | 31.96 | 4 | 32.12 | 272.12 | 271.96 | 272.12 | 272.07 | 0.09 | 62.46 |

Cannon-Fenske

| Density | | | | | | | | | |
|---------|---------------|---------------------------|-------------------------------|--------------------------------|----------------|-----------------|------------------|---|---|
| ID | PSI Sample ID | Mass Empty Pycnometer (g) | Mass Pycnometer and Water (g) | Mass Pycnometer and sample (g) | Mass Water (g) | Mass Sample (g) | Specific gravity | Density of Sample Solution (kg/m ³) | Density of sample solution (g/cm ³) |
| CB-23 | 2006-668-01 | 31.6814 | 59.1552 | 55.5812 | 27.4738 | 23.8998 | 0.86991 | 867.34 | 0.86734 |
| BR-40 | 2006-668-02 | 31.6737 | 59.0761 | 55.5818 | 27.4024 | 23.9081 | 0.87248 | 869.91 | 0.86991 |
| BR-60 | 2006-668-03 | 31.6737 | 59.0761 | 55.4711 | 27.4024 | 23.7974 | 0.86844 | 865.88 | 0.86588 |
| BR-1220 | 2006-668-04 | 31.6814 | 59.1552 | 55.5980 | 27.4738 | 23.9166 | 0.87052 | 867.95 | 0.86795 |

Cannon-Fenske

| ID | PSI Sample ID | Kinematic Viscosity (mm ² /s) | Density of sample solution (g/cm ³) | Viscosity (cPs) |
|---------|---------------|---|--|-----------------|
| CB-23 | 2006-668-01 | 208.02 | 0.86734 | 180.42 |
| BR-40 | 2006-668-02 | 304.97 | 0.86991 | 265.30 |
| BR-60 | 2006-668-03 | 502.72 | 0.86588 | 435.30 |
| BR-1220 | 2006-668-04 | 62.46 | 0.86795 | 54.21 |

Cannon-Fenske

| Cannon Viscosity Standard | | Flow Times (minute,second) | | | | | | | | | | Flow Times (seconds) | | | | St Dev |
|---------------------------|--------|----------------------------|--------|--------|--------|--------|--------|--------|---------|---------|---------|----------------------|------|--|--|--------|
| | | 1 | | 2 | | 3 | | 1 | 2 | 3 | Average | | | | | |
| | | | | | | | | | | | | | | | | |
| Viscometer | minute | second | minute | second | minute | second | minute | second | 1 | 2 | 3 | Average | | | | |
| N35 | F12 | 4 | 44.96 | 4 | 44.90 | 4 | 45.03 | | 284.96 | 284.90 | 285.03 | 284.96 | 0.07 | | | |
| N100 | F12 | 16 | 48.50 | 16 | 48.56 | 16 | 48.71 | | 1008.50 | 1008.56 | 1008.71 | 1008.59 | 0.11 | | | |
| N100 | P94 | 3 | 30.59 | 3 | 30.68 | 3 | 30.71 | | 210.59 | 210.68 | 210.71 | 210.66 | 0.06 | | | |
| S200 | P94 | 6 | 59.75 | 6 | 59.40 | 6 | 59.56 | | 419.75 | 419.40 | 419.56 | 419.57 | 0.18 | | | |

Cannon-Fenske

| Cannon Viscosity Standard | Viscometer | Kinematic Viscosity of Standard (mm ² /s) | Viscometer Constant | Viscometer Coefficient |
|---------------------------|------------|--|---------------------|------------------------|
| | | | C ₁ | C ₂ |
| N35 | F12 | 65.41 | 0.2293 | -18.38 |
| N100 | F12 | 231.3 | | |
| N100 | P94 | 231.3 | 1.1038 | 257.59 |
| S200 | P94 | 462.5 | | |

Values from manufacturer certificates of analysis

| Cannon-Fenske Viscometers | |
|---------------------------|--|
| Viscometer Size 300 | Viscometer Constant |
| F-12 | 0.2299 mm ² /s ² |
| Viscometer Size 400 | Viscometer Constant |
| P94 | 1.1045 mm ² /s ² |

Values Calculated from Viscosity Standards

| Cannon-Fenske Viscometer F12 | |
|------------------------------|----------------|
| C ₁ | C ₂ |
| | 0.2293 |
| | -18.38 |
| Cannon-Fenske Viscometer P94 | |
| C ₁ | C ₂ |
| | 1.1038 |
| | 257.59 |

Polimeri Europa

Page 1 of 1



LAVORARE

NOI

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POLIMERI EUROPA
L'AZIENDA

I PRODOTTI
E LE APPLICAZIONI

LA RETE DI VENDITA
E L'ASSISTENZA

LICENSING
DELLE TECNOLOGIE

SALUTE SICUREZZA
AMBIENTE

OPPORTUNITA'
DI LAVORO



LA RETE DI VENDITA
E L'ASSISTENZA



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DELLE TECNOLOGIE



Polimeri Europa S.p.A. Partita IVA: 01768800748



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PRODUCTS &
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SALES NETWORK
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TECHNOLOGY
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HEALTH, SAFETY &
ENVIRONMENT

LANGUAGE MAP MAIL DOWNLOAD

E-SBR_HSR S-SBR BR Synthetic Latexes
EPR NBR_NBR-PVC TPR PDF version

Polybutadiene Rubber (BR)

| Grades | CIS content % | Mooney viscosity ML(1+4) 100°C | Stabilizer | Main applications |
|------------------------|---------------|--------------------------------|--------------|--|
| High Cis Types | | | | |
| Europrene NEOCIS BR 40 | 98 | 43 | Non staining | Tyre tread and sidewall, camelback, conveyor belts, technical goods, hoses, golf balls |
| Europrene NEOCIS BR 60 | 98 | 63 | Non staining | |

| Grades | CIS content % | Mooney viscosity ML(1+4) 100°C | Stabilizer | Main applications |
|----------------------|---------------|--------------------------------|--------------|---|
| Low Cis Types | | | | |
| Intene 50 | 38 | 48 | Non staining | Tyres, belting, moulded and extruded articles |
| Intene P 30 AF | 38 | 50 | Non staining | |

| Grades | CIS content % | Viscosity cps 5% STY 25°C | Colour Alpha | STY insoluble % (325) filter | Stabilizer | Main applications |
|-------------------------------|---------------|---------------------------|--------------|------------------------------|---------------|--|
| Low Cis Types for HIPS | | | | | | |
| Intene 40 AF | 38 | 100 | 5 | 0.02 | Food approved | Specially prepared materials suitable for the manufacture of ABS and high impact polystyrene |
| Intene 50 A | 38 | 170 | 5 | 0.02 | Food approved | |

| | | | | | | |
|----------------------|----|-----|---|------|------------------|---|
| Intene 50 AM | 38 | 170 | 5 | 0.02 | Food approved | Specially prepared materials suitable for the manufacture of ABS and high impact polystyrene |
| Intene 50 AF | 38 | 170 | 5 | 0.02 | Food approved | |
| Intene 60 AF | 38 | 250 | 5 | 0.02 | Food approved | Specially prepared materials suitable for the manufacture of ABS, high impact and glossy |
| Intene P 30 AF | 38 | 45 | 5 | 0.02 | Food approved | |

Storage conditions: store in vented, dry area at temperatures between 20°C and 30°C; no direct sunlight.
Please consult the relevant safety data sheet for more detailed information.

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From: Jerry Fasolino Jr. [altrubber@altrubber.com]
Sent: Thursday, January 11, 2007 1:18 PM
To: Jenkins, Thomas
Subject: RE: BR products
Importance: High

Hello Tom,
Sorry for the delay. The following is from the technical manager at Polimeri Europa. I hope this answers your questions.

Referring to Acushnet questions, I confirm that both Neocis BR 40 and BR 60 have not changed in comparison to materials approved by them some years ago..

best regards
Mauro
Mauro Da Via
(Product&Technical Service manager BR/SBR)
phone: **390252032455 - fax: **390252042298
e-mail: mauro.da.via@polimerieuropa.com
Polimeri Europa S.p.A

Best Regards,

Jerry Fasolino Jr.
Alternative Rubber & Plastics, Inc.
200 Creekside Drive
Amherst, NY 14228
Phone: 716-691-2141
Fax: 716-691-5664
jerry@altrubber.com

From: Jenkins, Thomas [mailto:JenkinsT@howrey.com]
Sent: Thursday, January 11, 2007 12:45 PM
To: altrubber@altrubber.com
Subject: Jerry Fasolino Jr.

Mr. Fasolino,

Thank you for taking my call earlier this week relating to the Neocis 40 and 60 rubbers samples provided to Acushnet. I am following up on Auchnet's inquiry as to whether either of these rubbers have changed since they were formerly produced by Enichem.
Have you been able to contact Polimeri Europa with regards to this issue?

Thank you in advance for your assistance,

Tom Jenkins.
(312) 343-0570.

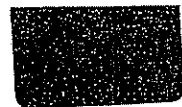
1/14/2007

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1/14/2007

EniChem America Inc.

1211 Avenue of the Americas
New York, NY 10036 Tel. (212) 382-6300



SECTION 1

Manufacturer's Name

EniChem Elastomeri SpA

MATERIAL SAFETY DATA SHEET

Product: Europrene Neocis

Issued: May, 1990

Supersedes: April, 1989

Address

Italy Office: EniChem Elastomeri S.p.A.
Strada 3 - Palazzo B1
20090 ASSAGO (Milano) - Italy

U.S.A. Office: EniChem America Inc.
1211 Avenue of the Americas
New York, New York 10036

Phone: Italy 39/2/5201
U.S.A. 212/382/6300

Chemical Name and Synonyms

Homopolymer of Butadiene CAS. No. 9003-17-2

Trade Name and Synonyms

Europrene Neocis

Chemical Family

Solution BR

SECTION II - HAZARDOUS INGREDIENTS

The product contains minor amounts of "non rubber" components (e.g., suspending agents, antifoaming agents) which are not considered hazardous ingredients.

During processing, emission of volatile components and possibly monomers can be observed (see Section V).

EniChem

SECTION III - PHYSICAL DATA

Boiling Point

Not applicable

Vapor Pressure (mm Hg)

Not Applicable

Specific Gravity (H2O=1)

0.91 g/cm3

Percent Volatiles by volume (%)

Volatiles are mostly water vapour, less than 1% (content)

Solubility in Water

Insoluble

Appearance and Odor

Solid rubbery material, packaged as bales, amber color. Characteristic odor.

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

Ignition Point

More than 300°C

Extinguishing Media

Standard extinguishing media can be used; e.g.: water, foam, ABC dry powder.

Special Fire Fighting Procedures

Material is combustible: after ignition it burns giving off flames and black smoke. It generates both carbon monoxide and carbon dioxide.

Because of high temperatures, there is also emission of volatile substances (monomers, oxidation products and others) which are irritant and combustible.

Gases are toxic.

In case of fire, no special procedures are required. Avoid smoke inhalation.

Self-contained breathing apparatus should be used.

Unusual Fire and Explosion Hazards

No unusual hazards expected.

SECTION V - HEALTH HAZARD DATA

Threshold Limit Value

- No evidence has been found to date of danger to human health induced by these products, when they are processed according to correct working procedures.
 - Stable under normal processing conditions. Emission of volatile components and possibly monomers can be observed at high temperature.
 - TLV Values of monomers (ACGIH 1984/85)
- 1-3 BUTADIENE : TLV-TWA : (1000)ppm = (2200)mg/m3
TLV-STEL : (1250)ppm = (2750)mg/m3
- 1-3 Butadiene is included in ACGIH 1984/85 intended changes list.
list.

Suggested values are:

TLV-TWA : 10 ppm A2 = 22 mg/m3 A2
A2 = suspected human carcinogen

Effect of Overexposure

None known, when normal safe processing procedures are used.

Emergency and First Aid Procedure

Not applicable

SECTION VI - REACTIVITY DATA

Stability

Stable

Hazardous Polymerization

Will not occur

Materials/Conditions to Avoid

Strong oxidizing agents

Hazardous Decomposition Products

Carbon monoxide, carbon dioxide and other organic compounds, on combustion (see section IV).

SECTION VII - SPILL OR LEAK PROCEDURES

Steps to be Taken in Case Material is Released or Spilled

Sweep or pick up

Waste Disposal Method

Landfill or incineration in accordance with federal, state and local regulations.

SECTION VIII - SPECIAL PROTECTION INFORMATION

Respiratory Protection

In case of fire or when TLV values of monomers are incidentally exceeded (see section V) use self contained breathing apparatus.

Ventilation

Efficient exhaust ventilation should always be provided in order to remove fumes or dust produced in the working area and to maintain the workplace atmosphere below the admitted limit values (see section V).

Protective Equipment

- Protective gloves should be worn when handling hot stock
- Safety glasses are recommended

SECTION IX - SPECIAL PRECAUTIONS

Precautions to be Taken in Handling and Storing

- In order to avoid possible fires, keep the product away from heat sources, sparks or flames.
- Product can accumulate static electricity, during processing therefore it may be necessary to use suitable earthing system for dissipating any charges that may develop.
- Avoid inhalation of smoke and vapour produced during hot processing.
- Personal hygiene is essential, including thoroughly washing hands before eating or using the toilet.

Avoid eating, drinking and smoking in working areas.

- It is advisable to avoid prolonged contact with skin and mucous membranes.

SECTION X - TRANSPORTATION REQUIREMENTS

These products are classified as not hazardous material by the Department of Transportation.

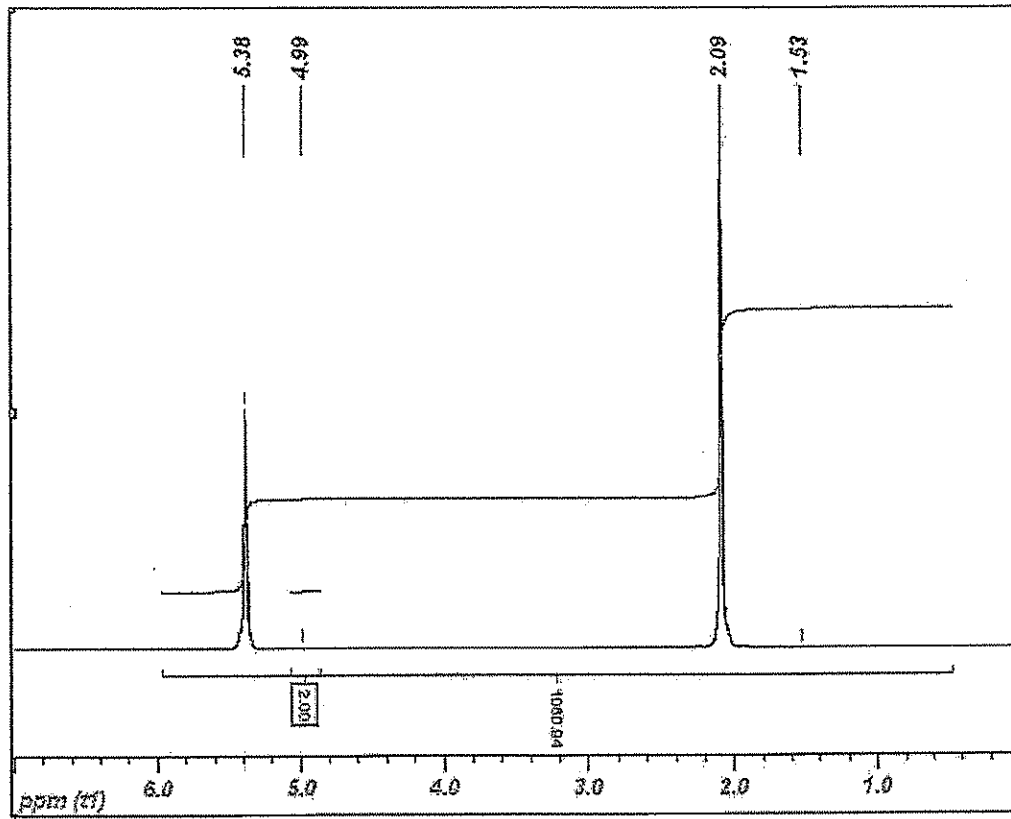
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The information and recommendations contained in this Safety Data Sheet have been compiled by ENICHEM ELASTOMERI SpA based on its best knowledge and the most reliable information available. No warranty, guarantee or representation is made by ENICHEM ELASTOMERI SpA as to the absolute correctness or sufficiency of any representation contained in this and other Safety Data Sheets and assumes no responsibility for the connection therewith; nor can it be assumed that all acceptable measures are contained in this and other Safety Data Sheets or that other or additional measures may not be required under particular exceptional conditions or circumstances.

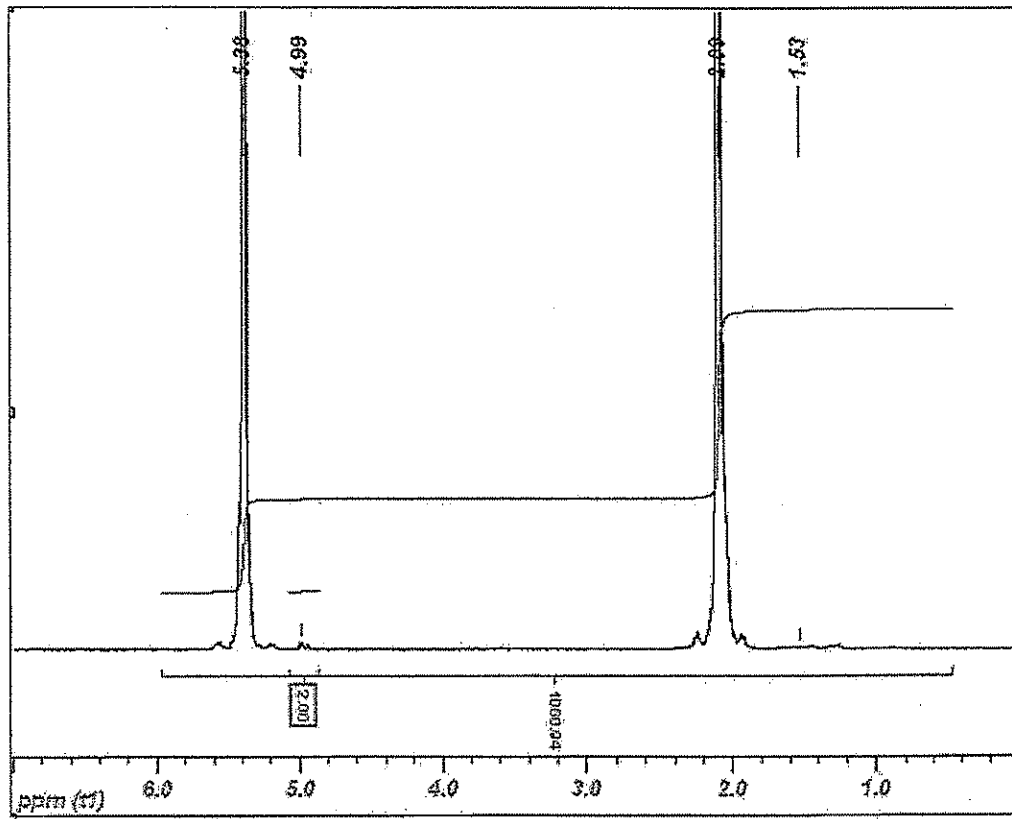
| ID | PSI Sample ID | Total integral of all sample signals | Integral of signal at 4.89 ppm | Number of protons on a repeat unit with resonances at 4.89 ppm | Total number of protons on a 1,2-poly(butadiene) repeat unit | Contribution to total integral from 1,2-poly(butadiene) | Weight Percent 1,2-butadiene |
|---------|---------------|--------------------------------------|--------------------------------|--|--|---|------------------------------|
| CB-23 | 2006-888-01 | 1050.94 | 2 | 2 | 6 | 6 | 0.57% |
| BR-40 | 2006-888-02 | 733.31 | 2 | 2 | 6 | 6 | 0.82% |
| BR-50 | 2006-888-03 | 723.15 | 2 | 2 | 6 | 6 | 0.83% |
| BR-1220 | 2006-888-04 | 445.83 | 2 | 2 | 6 | 6 | 1.35% |

Number of protons per repeat unit of 1,2-poly(butadiene) and 1,4-poly(butadiene) are equivalent
Formula weights of a single repeat unit of 1,2-poly(butadiene) and 1,4-poly(butadiene) are equivalent

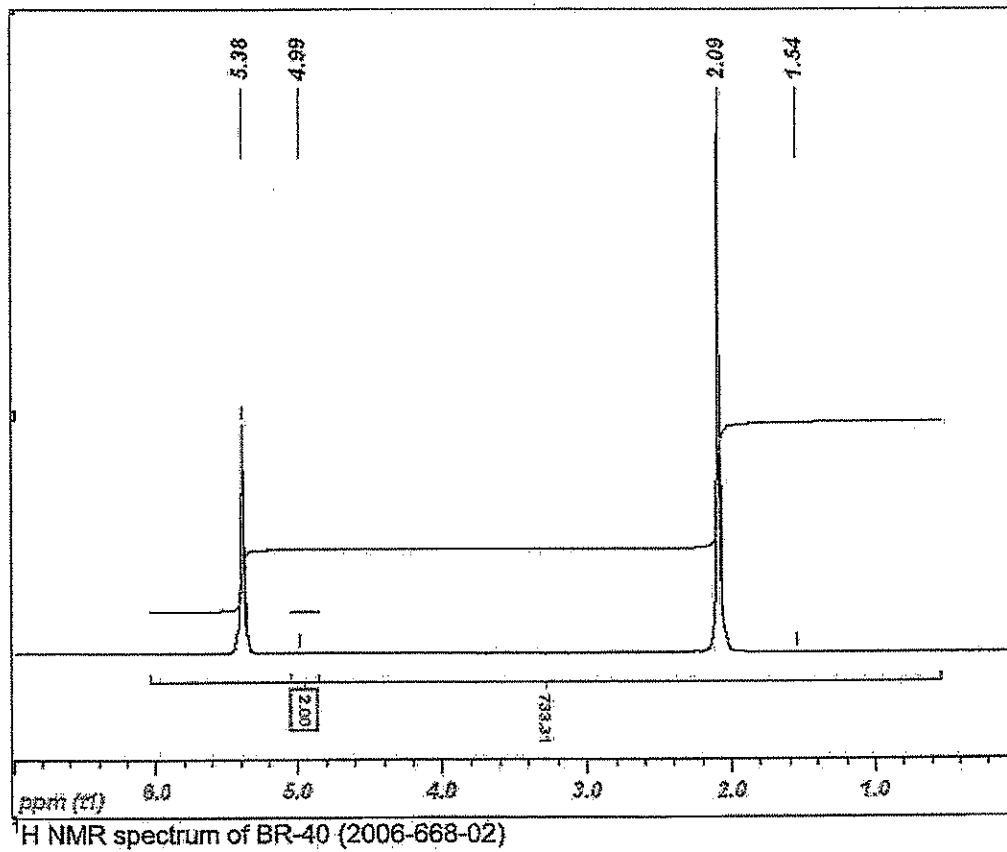
Weight Percent 1,2-butadiene
Calculated as (contribution to total integral from 1,2-polybutadiene) / (total integral of all sample signals)

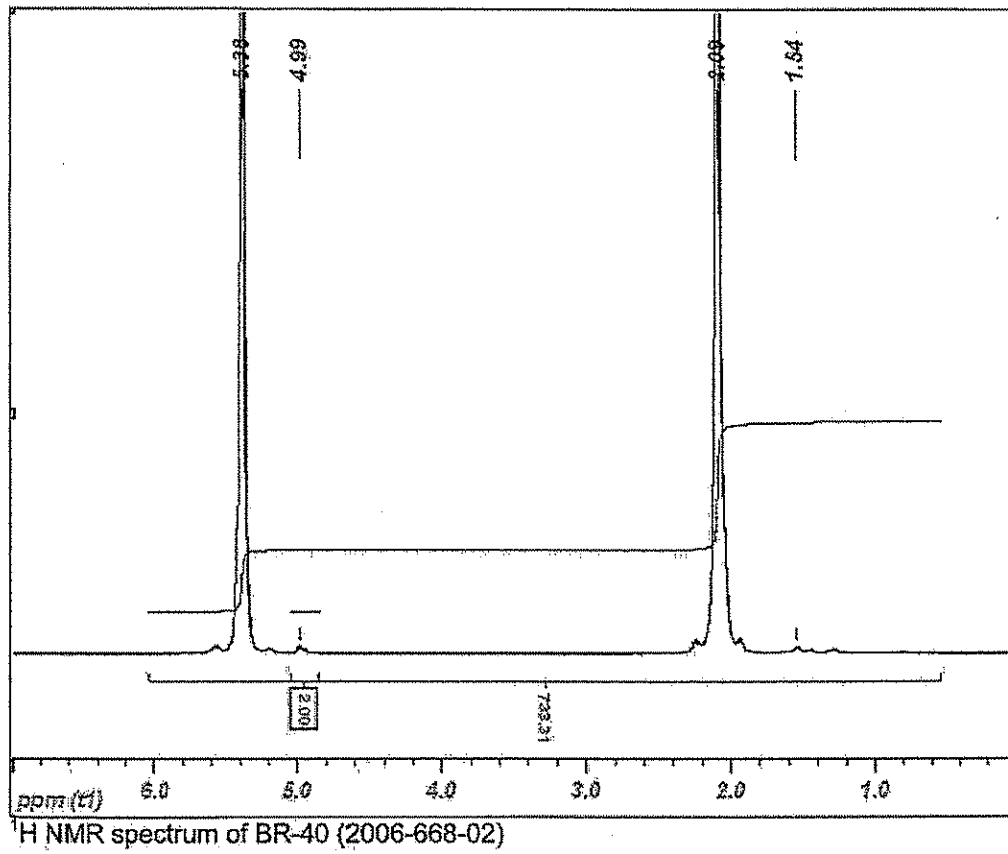


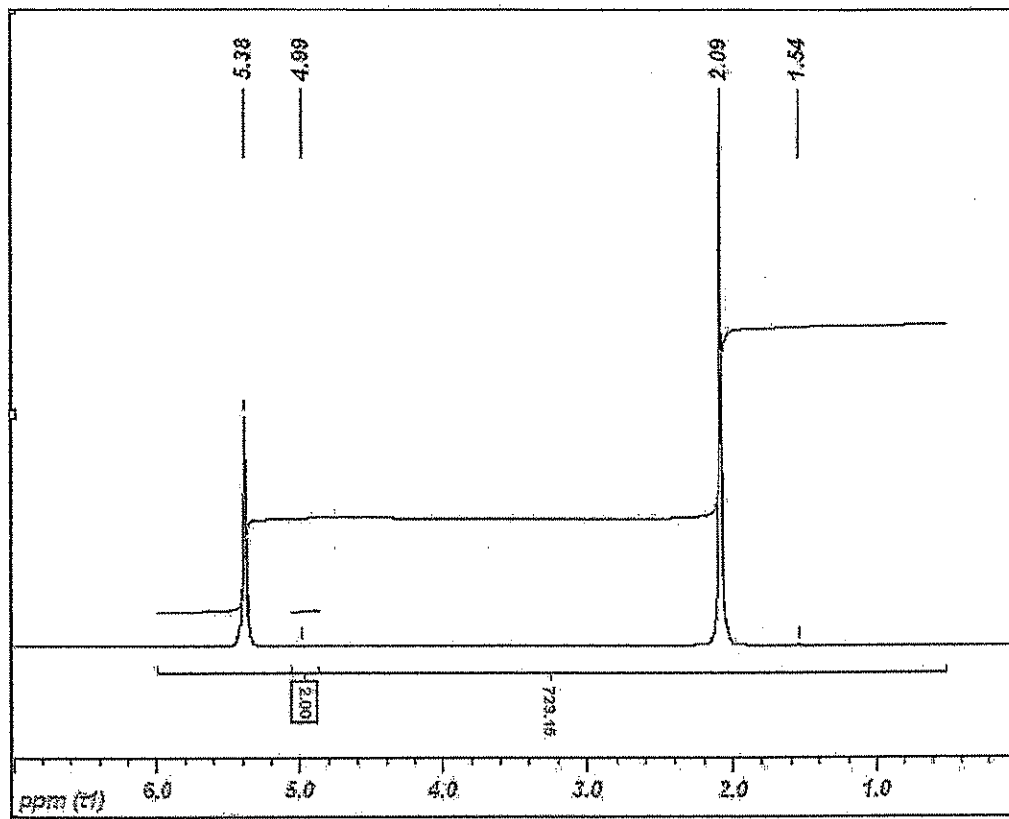
¹H NMR spectrum of CB23 (2006-668-01)



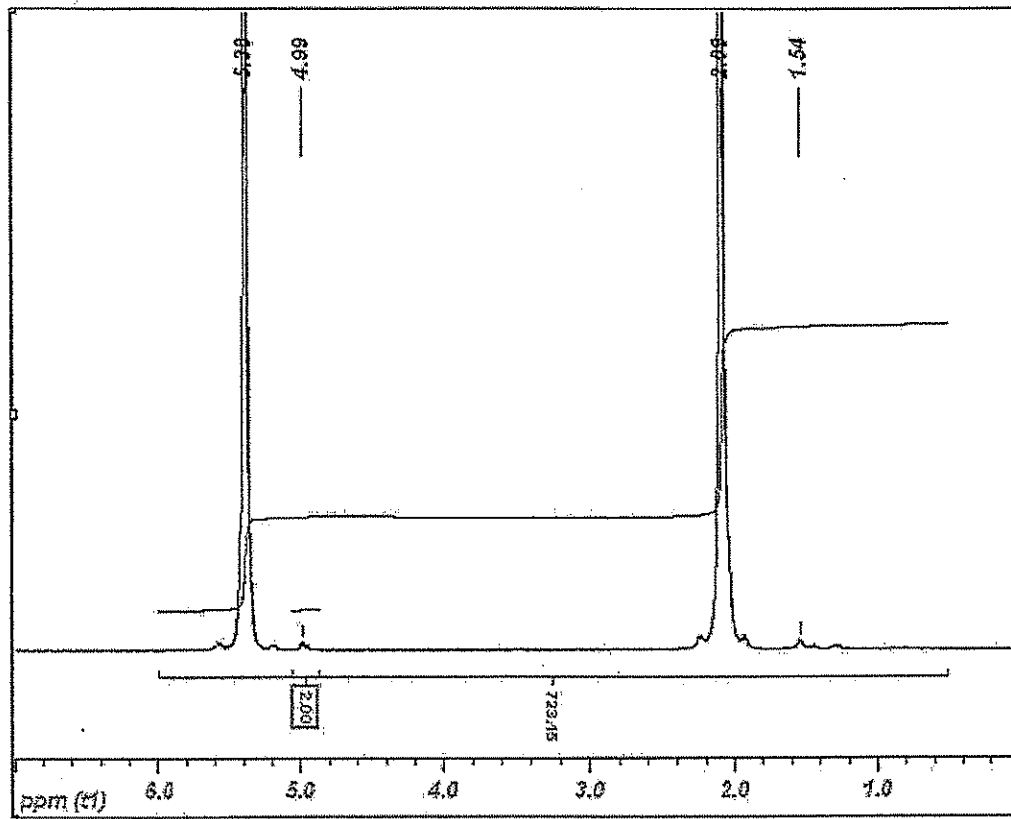
¹H NMR spectrum of CB23 (2006-668-01)



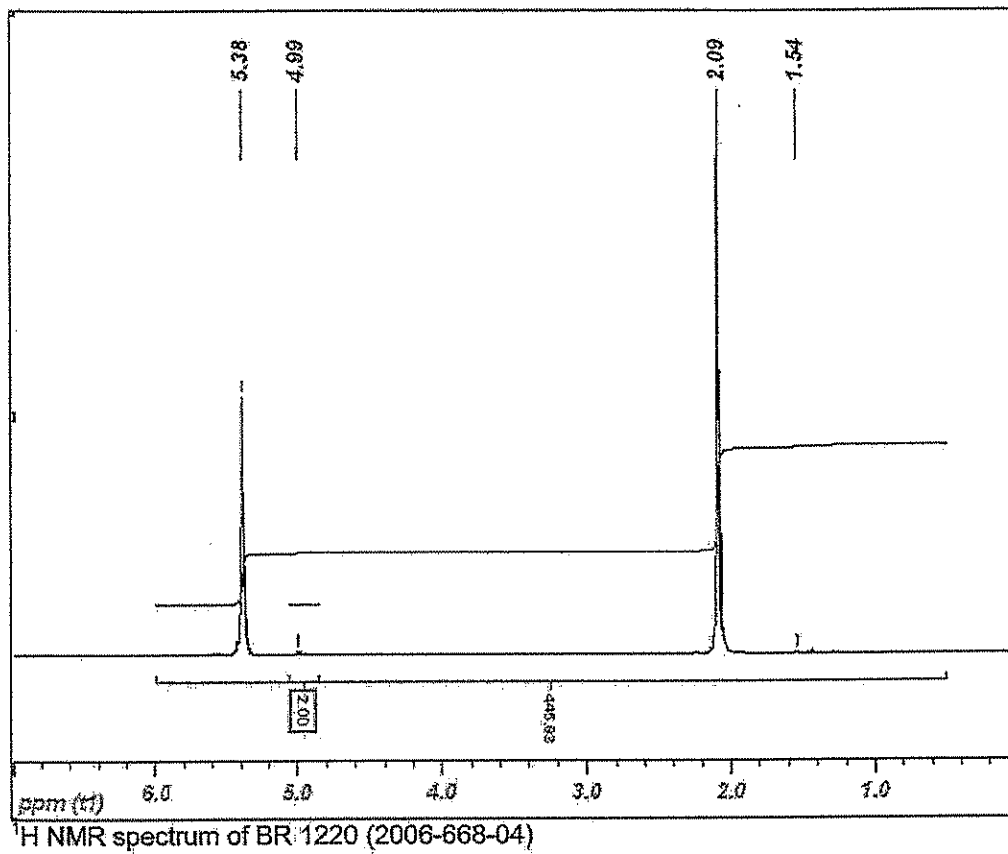


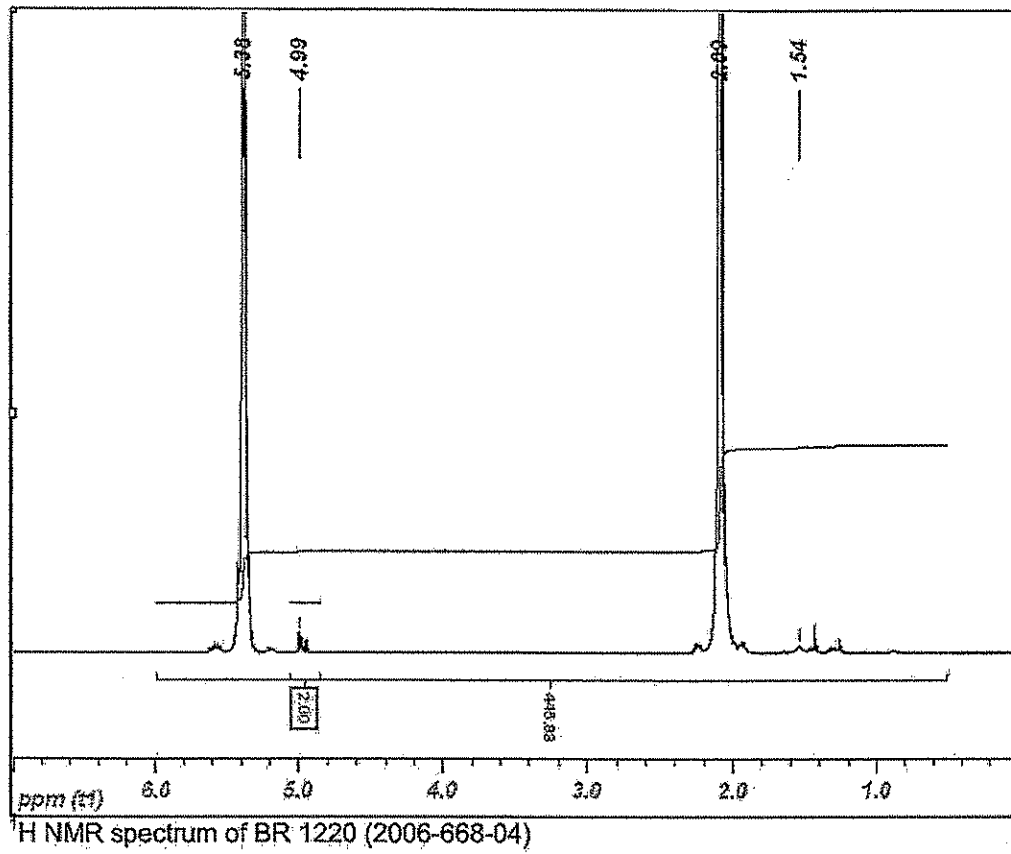


¹H NMR spectrum of BR-60 (2006-668-03)

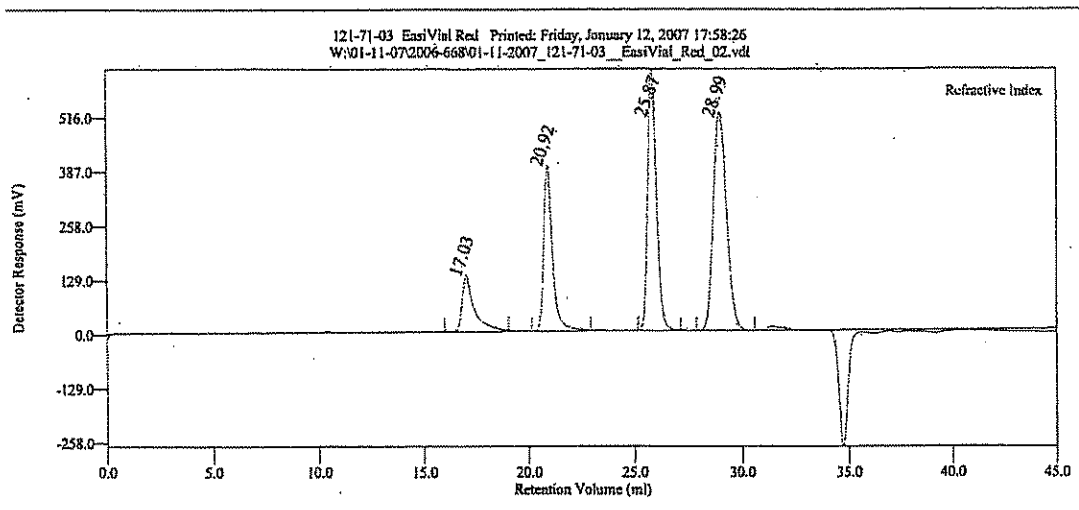


¹H NMR spectrum of BR-60 (2006-668-03)





| ID | PSI ID | Run | Mn (Daltons) | Mw (Daltons) | Mw/Mn (PDI) | |
|-------|-------------|-----|--------------|--------------|-------------|---------|
| | | | | | Value | Average |
| BR-40 | 2006-668-02 | A | 219,590 | 747,995 | 3.406 | 3.327 |
| | | B | 228,358 | 741,371 | 3.247 | |
| BR-60 | 2006-668-03 | A | 285,762 | 831,350 | 2.909 | 2.919 |
| | | B | 284,473 | 833,190 | 2.929 | |



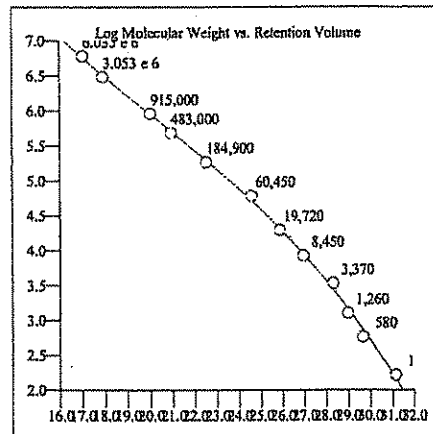
Calibration Results

$$\text{Log}(M_p) = A_0 + A_1 \cdot V_p + A_2 \cdot V_p^2 + A_3 \cdot V_p^3 + A_4 \cdot V_p^4 + A_5 \cdot V_p^5$$

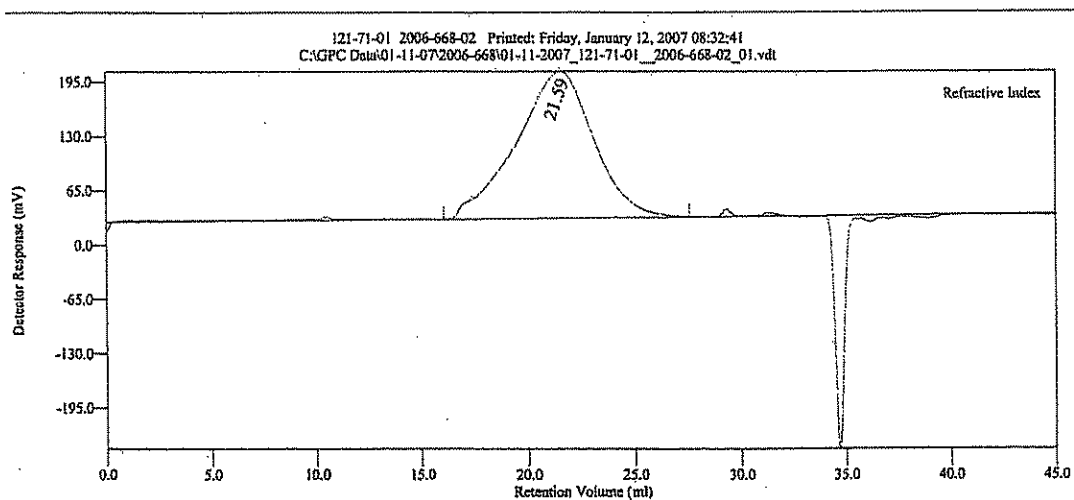
r-squared = 0.998421

| | |
|----|--------------|
| A0 | 17.4634 |
| A1 | -1.1812 |
| A2 | 0.0449 |
| A3 | -7.2900e-004 |
| A4 | 0.0000 |
| A5 | 0.0000 |

| Mp Std | Mc (Calc) | Difference | % Rel Diff |
|-----------|-----------|------------|------------|
| 6.035 e 6 | 5.729 e 6 | 305808.50 | 5.07 |
| 3.053 e 6 | 3.218 e 6 | -165257.75 | -5.41 |
| 915,000 | 891,696 | 23303.13 | 2.55 |
| 483,000 | 513,738 | -30738.38 | -6.36 |
| 184,900 | 195,733 | -10833.47 | -5.86 |
| 60,450 | 51,417 | 9032.82 | 14.94 |
| 19,720 | 20,293 | -573.12 | -2.91 |
| 8,450 | 8,700 | -250.53 | -2.96 |
| 3,370 | 2,710 | 659.73 | 19.58 |
| 1,260 | 1,439 | -179.38 | -14.24 |
| 580 | 723 | -142.57 | -24.58 |
| 162 | 143 | 18.98 | 11.71 |



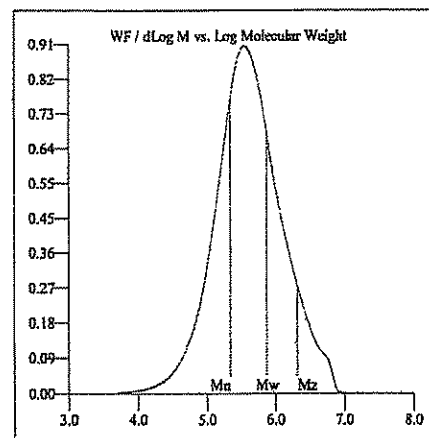
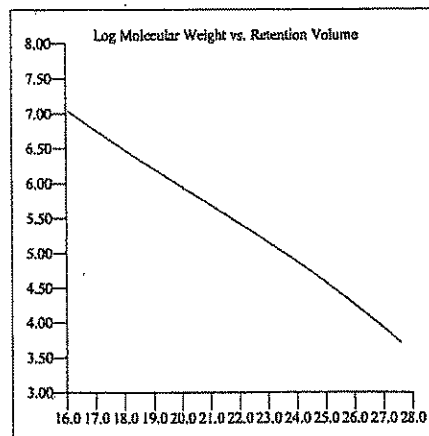
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|--------------------------|---|
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| Date Acquired | Jan 11, 2007 - 15:47:33 |
| Solvent | THF |
| Acquisition Operator | lin : |
| Calculation Operator | intodd : Jason Todd |
| Column Set | GMHHR-H x3 + Guard |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Ini Volume - (ul) | 150.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 30.0 |
| Column Temp. - (deg C) | 30.0 |
| OmniSEC Build Number | 224 |

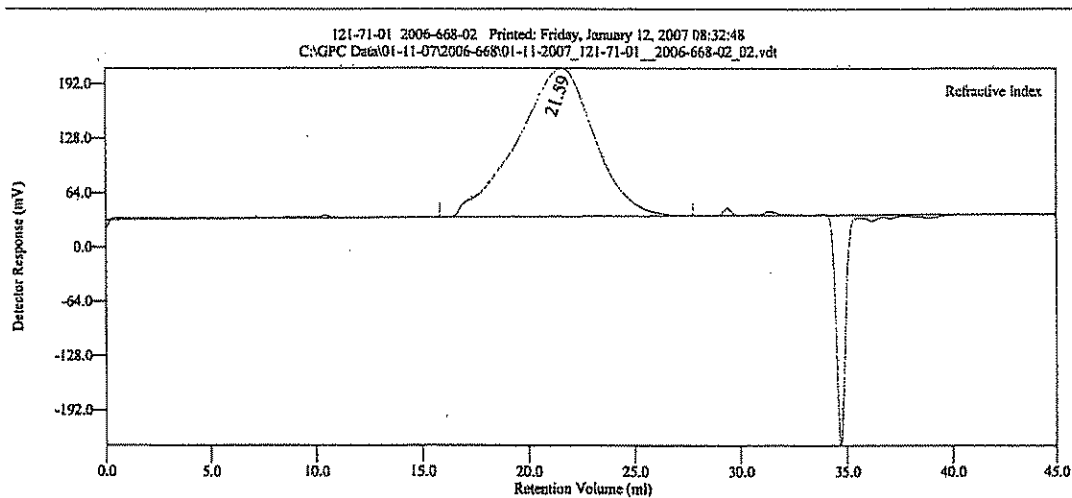


Conventional Calibration - Homopolymers : Results

| | |
|-------------------|-----------|
| Peak RV - (ml) | 21.587 |
| Mn - (Daltons) | 219,590 |
| Mw - (Daltons) | 747,995 |
| Mz - (Daltons) | 2,067 e 6 |
| Mo - (Daltons) | 343,394 |
| Mw / Mn | 3.406 |
| Percent Above Mw: | 0 |
| Percent Below Mw: | 0 |
| Mw 10.0% Low | 66,613 |
| Mw 10.0% High | 3,194 e 6 |
| RI Area - (mVml) | 754.13 |
| UV Area - (mVml) | 0.00 |

| | |
|--------------------------|--|
| Annotation | |
| Method File | convcal-0007.vem |
| Limits File | 7 121-71-01 2006-668-02_01-convcal-0007-0000.lim |
| Date Acquired | Jun 11, 2007 - 19:41:54 |
| Solvent | THF |
| Acquisition Operator | tim : Tim Rumpfolt |
| Calculation Operator | tim : Tim Rumpfolt |
| Column Set | GMHHR-H x3 + Guard |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Ini Volume - (ul) | 150.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 30.0 |
| Column Temp. - (deg C) | 30.0 |
| OmniSEC Build Number | 224 |

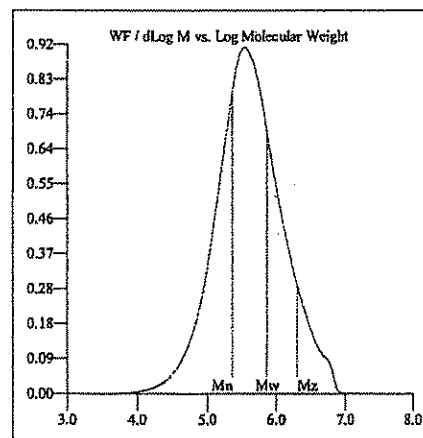
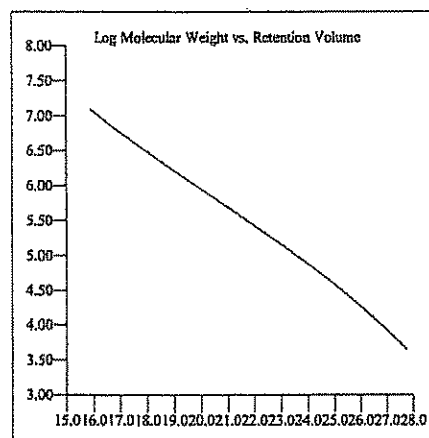


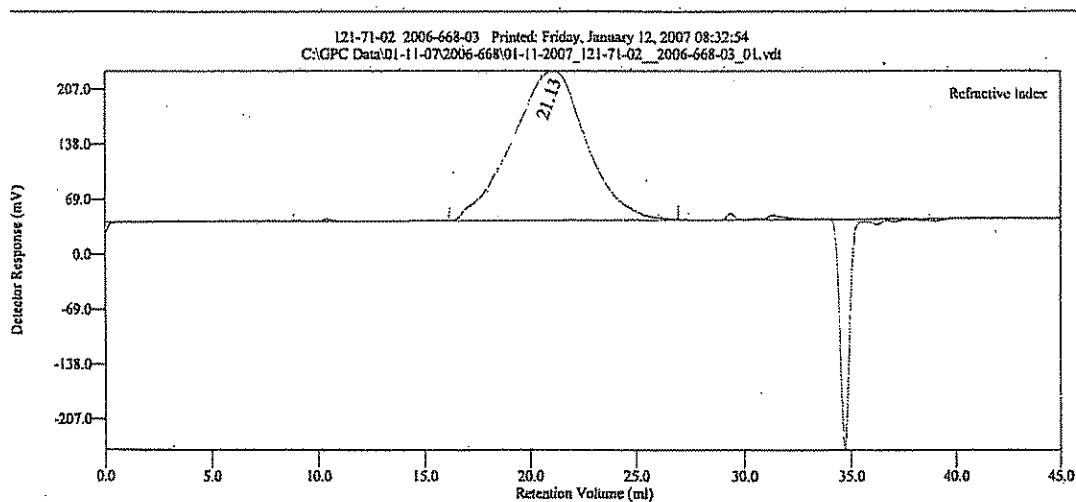


Conventional Calibration - Homopolymers : Results

| | |
|-------------------|-----------|
| Peak RV - (ml) | 21.590 |
| Mn - (Daltons) | 228,358 |
| Mw - (Daltons) | 741,371 |
| Mz - (Daltons) | 2,030 e 6 |
| Mp - (Daltons) | 342,372 |
| Mw / Mn | 3.247 |
| Percent Above Mw: | 0 |
| Percent Below Mw: | 0 |
| Mw 10.0% Low | 69,008 |
| Mw 10.0% High | 3,138 e 6 |
| RI Area - (mVmin) | 724.37 |
| UV Area - (mVmin) | 0.00 |

| Annotation | |
|--------------------------|--|
| Method File | convcal-0007.vcm |
| Limits File | 7 121-71-01 2006-668-02 02-convcal-0007-0000.lim |
| Date Acquired | Jan 11, 2007 - 20:28:45 |
| Solvent | THF |
| Acquisition Operator | tim : Tim Runfeldt |
| Calculation Operator | tim : Tim Runfeldt |
| Column Set | GMHHR-H x3 + Guard |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 150.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 30.0 |
| Column Temp. - (deg C) | 30.0 |
| OmniseC Build Number | 224 |

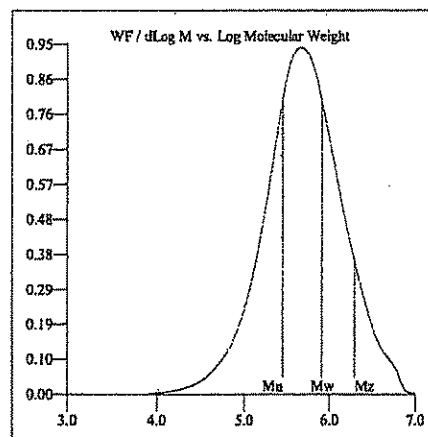
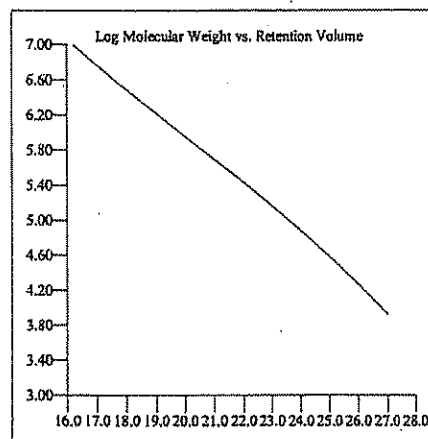


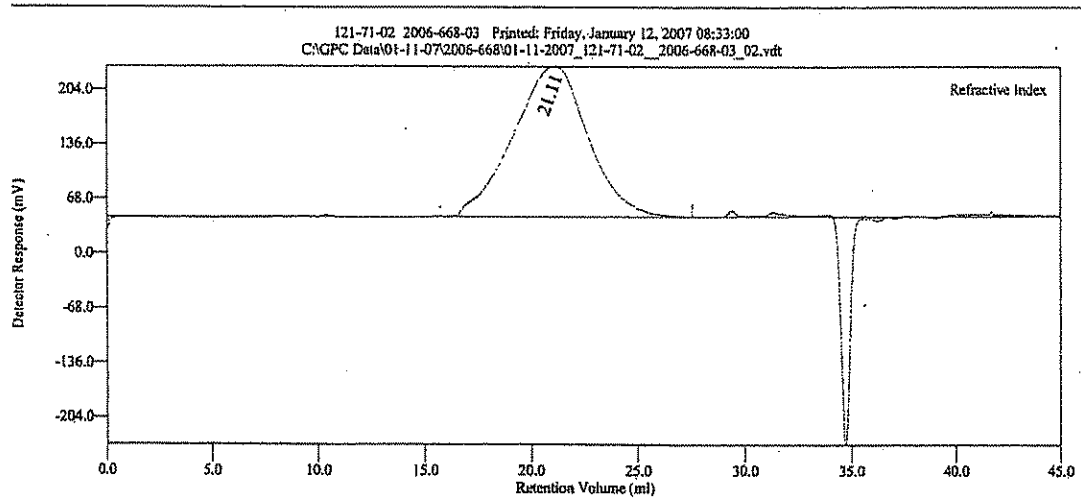


Conventional Calibration - Homopolymers: Results

| | |
|-------------------|-----------|
| Peak RV - (ml) | 21.130 |
| Mn - (Daltons) | 285,762 |
| Mw - (Daltons) | 831,350 |
| Mz - (Daltons) | 1.977 e 6 |
| Mp - (Daltons) | 452,681 |
| Mw / Mn | 2.909 |
| Percent Above Mw: | 0 |
| Percent Below Mw: | 0 |
| Mw 10.0% Low | 86,740 |
| Mw 10.0% High | 3.195 e 6 |
| R1 Area - (mvm) | 759.88 |
| UV Area - (mvm) | 0.00 |

| Annotation | |
|--------------------------|--|
| Method File | convcal-0007.vcm |
| Limits File | 07 121-71-02 2006-668-03 01-RAIS-0000-0001.lim |
| Date Acquired | Jan 11, 2007 - 21:15:37 |
| Solvent | THF |
| Acquisition Operator | tim : Tim Rumpf |
| Calculation Operator | tim : Tim Rumpf |
| Column Set | GMHHR-H x3 + Guard |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 150.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 30.0 |
| Column Temp. - (deg C) | 30.0 |
| OmniSEC Build Number | 224 |

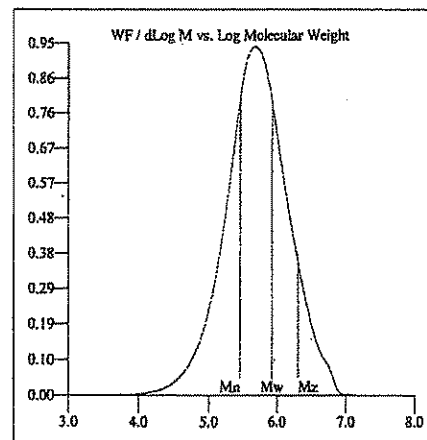
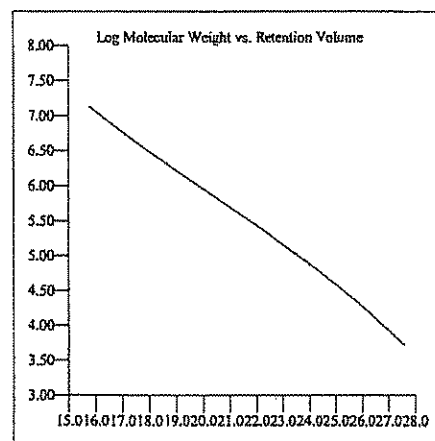


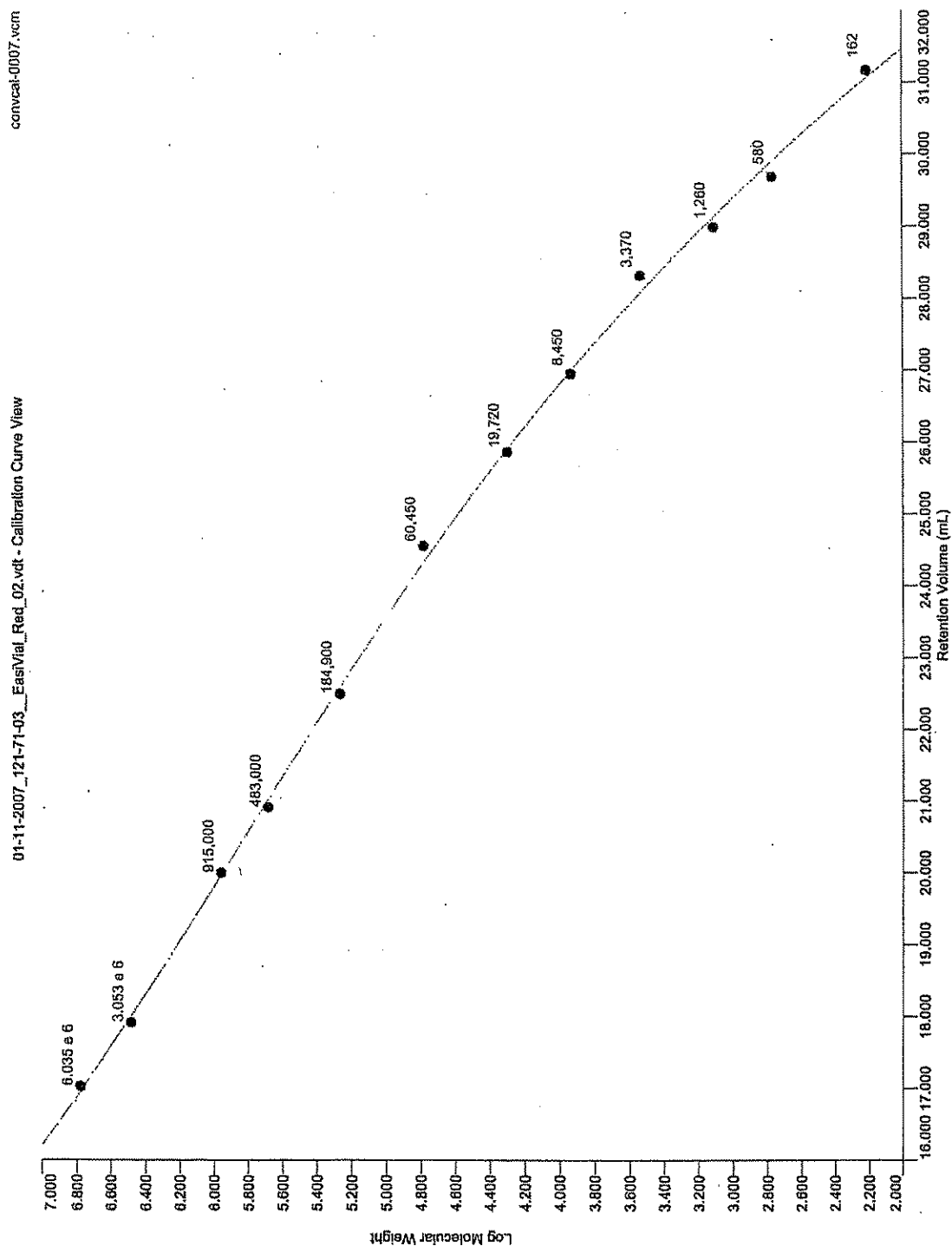


Conventional Calibration - Homopolymers : Results

| | |
|-------------------|-----------|
| Peak RV - (ml) | 21.110 |
| Mn - (Daltons) | 284,473 |
| Mw - (Daltons) | 833,190 |
| Mz - (Daltons) | 2.006 e 6 |
| Mp - (Daltons) | 458,087 |
| Mw / Mn | 2.929 |
| Percent Above Mw: | 0 |
| Percent Below Mw: | 0 |
| Mw 10.0% Low | 86,995 |
| Mw 10.0% High | 3.215 e 6 |
| RI Area - (mVmin) | 760.47 |
| UV Area - (mVmin) | 0.00 |

| | |
|--------------------------|--|
| Annotation | |
| Method File | convcal-0007.vcm |
| Limits File | 7 121-71-02 2006-668-03 02-convcal-0007-0000.lim |
| Date Acquired | Jan 11, 2007 - 22:02:28 |
| Solvent | THF |
| Acquisition Operator | tim : Tim Rumpfelt |
| Calculation Operator | tim : Tim Rumpfelt |
| Column Set | GMHHR-H x3 + Guard |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 150.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 30.0 |
| Column Temp. - (deg C) | 30.0 |
| OmniSEC Build Number | 224 |







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United States Patent [19]

Sarraf et al.

[11] **Patent Number:** 5,708,081[45] **Date of Patent:** Jan. 13, 1998

[54] **COMPOSITION COMPRISING A VINYLAROMATIC POLYMER AND A RUBBER AND PROCESS FOR OBTAINING IT**

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[52] **U.S. Cl.** 525/87; 525/316

[58] **Field of Search** 525/87, 316, 89, 525/98, 99

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Primary Examiner—Mark L. Warzel
Attorney, Agent, or Firm—Pennie & Edmonds

[57] **ABSTRACT**

The invention relates to polymer compositions of high impact strength, comprising a vinylaromatic polymer and a rubber, and to a process for their manufacture.

These compositions are obtained by virtue of the use of two polybutadienes whose viscosities, measured at 25° C. at a concentration of 5% in styrene, are, respectively, between 120 and 350 centipoises in the case of one and between 30 and 90 centipoises in the case of the other.

27 Claims, No Drawings

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COMPOSITION COMPRISING A VINYLAROMATIC POLYMER AND A RUBBER AND PROCESS FOR OBTAINING IT

TECHNICAL FIELD

The invention relates to polymer compositions comprising a vinylaromatic polymer and a rubber. These compositions are easy to process and exhibit good gloss and excellent mechanical properties.

They find applications in fields as diverse as electrical household appliances, that of office equipment or packaging.

PRIOR ART

Various techniques for improving the impact strength of compositions based on vinylaromatic polymer and rubber have been proposed.

Document EP 418,042 teaches an impact polystyrene composition comprising a branched polybutadiene exhibiting a double distribution of molecular masses, the ratio of the mean molecular masses of the component of high masses to that of low masses being higher than a factor of 2.5 and preferably between 3 and 5. The component of high molecular masses corresponds to branched molecules, while the component of low molecular masses corresponds to incompletely branched molecules. The polybutadiene has a cis-1,4 structure content which is preferably lower than 70% and more preferably lower than 50%.

The impact polystyrenes thus obtained have a marked bimodal structure and the distribution of their particle diameters indicates the presence of three distinct particle populations.

Document JP 4-100810 teaches the use of a mixture of two polybutadienes exhibiting very different viscosities. One of these polybutadienes must exhibit an intrinsic viscosity of between 3 and 7 dl/g, whereas the other polybutadiene must exhibit an intrinsic viscosity of between 0.5 and 1.4 dl/g. The use of such polybutadienes exhibits limits. In fact, the manufacture of a polybutadiene whose intrinsic viscosity is close to 7 dl/g is difficult to carry out. In addition, if the viscosity of the second polybutadiene is close to 1.4 dl/g, the viscosity of the polymer solution, which also contains the first polybutadiene of particularly high viscosity, becomes too high.

DESCRIPTION OF THE INVENTION

Polymer compositions comprising a vinylaromatic polymer and a rubber have now been found, the said rubber being derived from a high-viscosity polybutadiene and from a low-viscosity polybutadiene, the intrinsic viscosities of these two polybutadienes being close but different and such that that of the high-viscosity polybutadiene is lower than 3 dl/g and that of the low-viscosity polybutadiene is higher than 1.4 dl/g. The term rubber denotes the elastomeric phase present in the composition according to the invention.

This elastomeric phase contains all the mass of the polybutadienes initially introduced. The rubber of the compositions according to the invention therefore contains polybutadiene which may be partially crosslinked or grafted onto the vinylaromatic polymer. This rubber forms the shell of particles containing a proportion of the vinylaromatic polymer, the said particles themselves being dispersed in a matrix of vinylaromatic polymer.

The use of the two polybutadienes, of high and low viscosity, produces polymer compositions with remarkable

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mechanical properties, in particular with regard to the impact strength. These properties are generally superior to those obtained by employing only one of these polybutadienes, with an appreciably identical polybutadiene content and with an appreciably identical degree of grafting of the polybutadiene with the vinylaromatic polymer in the polymer compositions being considered.

Furthermore, a polymer composition according to the invention exhibits an impact strength which is higher than the arithmetic mean of the impact strengths of the compositions obtained, on the one hand, with the high-viscosity polybutadiene by itself and, on the other hand, with the low-viscosity polybutadiene by itself, this being at a polybutadiene content which is appreciably identical and with an appreciably identical degree of grafting of polybutadiene with vinylaromatic polymer in the polymer compositions being considered.

This is reflected in the fact that if

P denotes the impact strength of a composition C according to the invention, in which the rubber is derived from a high-viscosity polybutadiene X and from a low-viscosity polybutadiene Y, x denoting the percentage by weight of X relative to the total weight of polybutadiene introduced and y denoting the percentage by weight of Y relative to the total weight of polybutadiene introduced,

P_x denotes the impact strength of a composition C_x comprising the same vinylaromatic polymer as C and a rubber obtained exclusively from X, the polybutadiene content in C_x being here identical with the polybutadiene content in C, the degrees of grafting of the polybutadienes in C and C_x being appreciably identical,

P_y denotes the impact strength of a composition C_y comprising the same vinylaromatic polymer as C and a rubber obtained exclusively from Y, the polybutadiene content in C_y being here identical with the polybutadiene content in C, the degree of grafting of the polybutadienes in C and C_y being appreciably identical,

there is a relationship P >

$$\frac{xP_x + yP_y}{x + y}$$

In addition, a composition according to the invention generally exhibits mechanical properties which are superior to those obtained by the use of a single polybutadiene whose viscosity is comparable with the viscosity of a mixture of the polybutadienes employed for producing the said composition, the said mixture containing the high- and low-viscosity polybutadienes in proportions which are identical with those employed for the production of the composition according to the invention, the degrees of grafting of the polybutadienes in the polymer compositions being considered being appreciably identical.

This last comparison with a single polybutadiene is meaningful only if the latter itself is not a mixture of different polybutadienes and, in any event, exhibits a polydispersity, that is to say a ratio of its mass-average molecular mass to its number-average molecular mass, lower than 4.

The high-viscosity polybutadiene is of linear structure, has a cis-1,4 structure content higher than 80% and preferably higher than 90% and exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 120 to 350 centipoises and preferably from 180 to 300

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centipoises. The low-viscosity polybutadiene is of linear, branched or star-shaped structure, has a cis-1,4 structure content lower than 80% and preferably between 30 and 60% and exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 30 to 90 centipoises and preferably from 40 to 75 centipoises.

The high-viscosity polybutadiene preferably exhibits a 1,2-vinyl structure content ranging from 0.1 to 5% and more preferably from 0.5 to 3%.

The low-viscosity polybutadiene preferably exhibits a 1,2-vinyl structure content ranging from 1 to 25% and more preferably from 5 to 18%.

The use of the polybutadienes described above is preferably carried out so that the high-viscosity polybutadiene represents 10 to 90% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 10% by weight of the total polybutadiene introduced.

Preferably, also, the use of the polybutadienes described above is carried out so that the high-viscosity polybutadiene represents 10 to 70% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 30% by weight of the total butadiene introduced.

The compositions according to the invention preferably contain polybutadiene in a proportion of 2 to 25%. This includes all the polybutadiene present in the compositions, either in a partially crosslinked form or in a form grafted onto the vinylaromatic polymer, the grafted vinylaromatic polymer itself not being included in the percentage of polybutadiene shown above.

The vinylaromatic polymer is obtained by the polymerization of at least one vinylaromatic monomer described below. It may therefore be a copolymer.

It is not ruled out that the polymer composition may contain the adjuvants which are usual in vinylaromatic polymers, such as at least one antioxidant and/or at least one plasticizer.

Another subject of the invention relates to a process for the manufacture of the polymer compositions described above.

The process according to the invention, which can function continuously or noncontinuously, comprises a stage of polymerization of at least one vinylaromatic monomer in the presence of high- and low-viscosity polybutadienes described above.

This polymerization stage maybe a suspension or bulk polymerization process, the principle of these two techniques being well known to a person skilled in the art. In the case of the polymerization must take place in bulk the polybutadienes are first of all dissolved in at least one vinylaromatic monomer, optionally in the presence of an organic solvent, and a polymerization is then carried out, the initiation of which may be thermal or using peroxide. If its initiation is thermal, this polymerization may be conducted between 110° and 180° C. and preferably between 120° and 160° C. If the initiation of the polymerization uses peroxide, the polymerization will be generally conducted between 70° and 180° C. and preferably between 90° and 160° C. During this polymerization stage the vinylaromatic monomer is polymerized either by itself or with a proportion of the polybutadienes and in this latter case grafting is said to take place between the polybutadienes and the vinylaromatic monomer and, in addition, the polybutadienes are partially crosslinked.

During these reactions the well-known phenomenon of phase inversion takes place, resulting in the formation of particles dispersed in vinylaromatic polymer.

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The stirring must be sufficient for this dispersion of particles to be uniform.

Following the polymerization stage it is appropriate to proceed to the removal of the volatile species such as unreacted monomers and possibly solvent. This may be carried out using conventional techniques such as by the use of a devolatilizer operating with heating and under vacuum.

The final polybutadiene and vinylaromatic polymer content of the composition according to the invention depends on the degree of progress of the polymerization carried out before removal of the volatile species. In fact, if the degree of progress of polymerization is low, the removal of the volatile species will result in the removal of a large quantity of vinylaromatic monomer and the final polybutadiene content of the composition will be higher. In order not to produce an excessively high crosslinking of the polybutadienes it is preferable not to force the polymerization of the vinylaromatic monomers to 100%.

The progress of the polymerization can be followed by virtue of samples taken during the polymerization stage and by determining the solids content on the samples withdrawn. The solids content means the percentage by weight of solid obtained after evaporation of the withdrawn samples in a vacuum of 25 mbar for approximately 20 minutes at 200° C., in relation to the initial weight of the sample. This treatment removes from the withdrawn sample the vinylaromatic monomers unpolymersized at the time of the withdrawal. The polymerization can be taken further, for example until a solids content of 70 or 80% is obtained.

At least one adjuvant or polymerization initiator, these being conventional in this kind of preparation, may be added to the polymerization mixture before or during the polymerization. These adjuvants may be plasticizers such as mineral oils, butyl stearate or dioctyl phthalate, stabilizers such as antioxidants, which may be phenol substituted by an alkyl group, such as di-tert-butyl-para-cresol, or phosphites such as trinonyl phenylphosphite.

A plasticizing oil may be introduced, generally in a proportion such that it is present in the final composition in a ratio of 0 to 8% by weight and preferably in a ratio of 0 to 5% by weight.

The polymerization initiators which are optionally added are those usually employed for this kind of preparation. They may be chosen from peroxides such as dibenzoyl peroxide, tert-butyl peroxybenzoate and 1,1-bis(tert-butylperoxy)cyclohexane.

Vinylaromatic monomer is intended to mean styrene, styrene substituted by an alkyl group on the vinyl group, such as alpha-methylstyrene or alpha-ethylstyrene, styrene substituted by an alkyl group on the ring, such as ortho-vinyltoluene, para-vinyltoluene, ortho-ethylstyrene or 2,4-dimethylstyrene, styrene substituted by a halogen on the ring, such as, for example, 2,4-dichlorostyrene, and styrene substituted both by a halogen and an alkyl group, such as 2-chloro-4-methylstyrene, as well as vinylanthracene. Styrene is a preferred vinylaromatic monomer.

The polymerization may be conducted in the presence of an organic solvent. This solvent will be chosen so that it does not boil under polymerization conditions and so that it is miscible with the vinylaromatic monomer and the vinylaromatic polymer derived therefrom. It is possible to employ alicyclic hydrocarbons such as cyclohexane or, preferably, aromatics such as toluene, benzene, ethylbenzene or xylene.

In general, the quantity of solvent which is employed will be such that the polymerization mixture does not contain more than 40% by weight of organic solvent.

EMBODIMENTS OF THE INVENTION

In the examples which follow, the structure and the properties of the polymer compositions obtained have been determined by the following techniques:

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melt flow index: ISO standard 1133 condition H
 1-kg Vicat point: ISO standard 306 A
 notched Izod impact strength: ISO standard 180/1A
 elasticity modulus measured in flexure: ISO standard 178
 tensile and flexural strength: ISO standard R527
 molecular mass of the polystyrene: the polystyrene is extracted from the impact polystyrene using methyl ethyl ketone and its molecular mass is measured by gel permeation chromatography (GPC).

In Table 1 Mw denotes the weight-average molecular mass of the polystyrene, Mn denotes the number-average molecular mass of the polystyrene and Mw/Mn denotes the ratio of the weight-average molecular mass to the number-average molecular mass of the polystyrene.

swelling ratio and residue content 0.4 grams of impact polystyrene are placed in 40 ml of toluene at ambient temperature with stirring for two hours. The composition thus obtained is then centrifuged at 20,000 revolutions per minute for 30 minutes so as to make it possible to separate off the gel formed from the solution. The wet (toluene-impregnated) gel obtained after separation from the solution is then dried in vacuum at 80° C. and a dry gel is obtained.

If Mh denotes the mass of wet gel, Md the mass of dry gel and Mt the mass of the impact polystyrene test sample, the swelling index SI is given by the formula $SI = Mh/Md$ and the residue content Cr, expressed as percentage by weight, is given by the formula $Cr = Md/Mt \times 100$.

The residue content indicates approximately the rubber content of the polymer composition since it adds the total percentage by weight of polybutadiene and the percentage by weight of polystyrene grafted to polybutadiene in the polymer composition.

Two compositions exhibiting an identical residue content and an identical polybutadiene content will therefore be considered as exhibiting an identical degree of grafting between the polybutadiene and the polystyrene.

polybutadiene content in the compositions: NF standard T 51-007

mean size of the rubber particles: by sedimentation particle size determination (capa 700) after dissolving in methyl ethyl ketone.

In the tables, the line "HV/LV" gives the relative percentage by weight of high-viscosity polybutadiene ("HV") and of low-viscosity polybutadiene ("LV").

EXAMPLE 1

Into a 15-litre reactor fitted with a mechanical stirrer and a temperature control are introduced 7.9 kg of styrene, 1.2 kg of ethylbenzene and 300 grams of a plasticizing oil with a viscosity of 210 centipoises at 20° C., of Primol 352 trademark, marketed by Esso.

300 grams of a first polybutadiene of trademark BR 1202 G, marketed by Shell, are then introduced at ambient temperature and with stirring in the form of gummy solid pieces, the said polybutadiene being of linear structure and exhibiting a viscosity of 160 centipoises at 25° C. at a concentration of 5% in styrene and an intrinsic viscosity of 2.5 dl/g at 25° C., a weight-average molecular mass of 287 000, a cis-1,4 structure content of 96.5, followed by 300 grams of a second polybutadiene of trademark P 1001, marketed by Enichem, in the form of gummy solid pieces, the said polybutadiene being of branched structure and exhibiting a viscosity of 45 centipoises at 25° C. at a concentration of 5% in styrene and an intrinsic viscosity of 1.9 dl/g at 25° C., a

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weight-average molecular mass of 175 000, a cis-1,4 structure content of 45% and a 1,2-vinyl structure content of 11%.

The two polybutadienes were therefore introduced into the reactor in equal quantity. By way of guidance it is mentioned that an equal parts mixture of these two polybutadienes exhibits a viscosity of 120 centipoises at 25° C. at a concentration of 5% in styrene.

After the polybutadiene has dissolved completely, thermal polymerization of the solution is started. The progress of the polymerization is followed by measuring the solids content obtained from withdrawals taken during the polymerization. The solids content corresponds to the percentage by weight of solid obtained after vacuum evaporation at 200° C. of the samples withdrawn, relative to the initial weight of the sample.

The reactor is first of all heated to 126° C. until a solids content of 27% is obtained. The temperature is then raised from 126° to 157° C. over 90 minutes. The solids content at this time is approximately 70%. The content of the reactor is then transferred to a devolatilizer at approximately 180° C. under vacuum, for approximately 10 minutes so as to extract the unpolymerized styrene and the ethylbenzene. The product obtained is granulated in a manner which is known to a Person skilled in the art. Specimens are produced by injection moulding for carrying out the mechanical tests. The results are collated in Table 1. The impact polystyrene obtained exhibits a monomodal particle size distribution with a maximum at about 1 µm.

EXAMPLE 2

Example 1 is repeated, except that 150 grams of the first polybutadiene and 450 grams of the second polybutadiene are introduced. The results are collated in Table 1.

EXAMPLE 3 (Comparative)

Example 1 is repeated, except that the 300 grams of the first polybutadiene and the 300 grams of the second polybutadiene are replaced with 600 grams of a linear polybutadiene of trademark HX 529C, marketed by Bayer, with a viscosity of 140 centipoises at 25° C. at a concentration of 5% in styrene and intrinsic viscosity of 2.1 dl/g at 25° C., with a weight-average molecular mass of 224 000, polydispersity of 1.26, cis-1,4 structure content of 38% and 1,2-vinyl structure content of 11%. The results are collated in Table 1.

EXAMPLE 4

Into a 15-litre reactor fitted with a mechanical stirrer and a temperature control are introduced 9 kg of styrene, 0.6 kg of ethylbenzene, 0.2 kg of a plasticizing oil with a viscosity of 210 centipoises at 20° C., of Primol 352 trademark, marketed by Esso.

200 grams of a first polybutadiene of trademark BR 1202G, marketed by Shell, are then introduced at ambient temperature and with stirring in the form of gummy solid pieces, the said polybutadiene being of linear structure and exhibiting a viscosity of 160 centipoises at 25° C. at a concentration of 5% in styrene and an intrinsic viscosity of 2.5 dl/g at 25° C., a weight-average molecular mass of 287 000, a cis-1,4 structure content of 96.5%, followed by 200 grams of a second polybutadiene of trademark HX 565SIC, marketed by Bayer, in the form of gummy solid pieces, said polybutadiene being of branched structure and exhibiting a viscosity of 40 centipoises at 25° C. at a concentration of 5%

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in styrene and an intrinsic viscosity of 1.7 dl/g at 25° C., a weight-average molecular mass of 165 000, a cis-1,4 structure content of 37% and a 1,2-vinyl structure content of 11%.

After the polybutadiene has dissolved completely, thermal polymerization of the solution is started in a way identical with the polymerization procedure described in Example 1. The results are collated in Table 1.

EXAMPLE 5 (comparative)

The procedure is as in Example 4, except that the 200 grams of the second polybutadiene are replaced with 200 grams of a linear polybutadiene of trademark H 529C marketed by Bayer, exhibiting a viscosity of 120 centipoises at 25° C. at a concentration of 5% in styrene and an intrinsic viscosity of 2.1 dl/g at 25° C., a weight-average molecular mass of 224 000, a cis-1,4 structure content of 38% and a 1,2-vinyl structure content of 11%. The results are collated in Table 1.

EXAMPLE 6 (comparative)

The procedure is as in Example 1, except that 600 grams of the first polybutadiene are introduced and no second polybutadiene.

The results are collated in Table 2.

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EXAMPLE 7 (comparative)

The procedure is as in Example 1, except that 600 grams of the second polybutadiene are introduced and no first polybutadiene.

The results are collated in Table 2.

EXAMPLE 8

The procedure is as in Example 1, except that 60 grams of the first polybutadiene and 540 grams of the second polybutadiene are introduced.

The results are collated in Table 2.

EXAMPLE 9

The procedure is as in Example 1, except that 420 grams of the first polybutadiene and 180 grams of the second polybutadiene are introduced.

The results are collated in Table 2.

EXAMPLE 10

The procedure is as in Example 4, except that the 200 grams of polybutadiene of trademark BR 1202 G are replaced with 200 grams of a polybutadiene of trademark BR 40 marketed by Enichem, the latter polybutadiene having a cis-1,4 structure content higher than 98% and a viscosity of 330 centipoises at 25° C. at a concentration of 5% in styrene.

The results are collated in Table 2.

TABLE 1

| UNIT | | | EXAMPLE 1 | EXAMPLE 2 | EXAMPLE 3 (comparative) | EXAMPLE 4 | EXAMPLE 5 (comparative) |
|---------------------------------------|------------------------------|-----------------------|-----------|-----------|----------------------------|-----------|----------------------------|
| Structure of the polymer compositions | Polybutadiene content | weight % | 8.2 | 8.5 | 8.4 | 6.3 | 6.1 |
| | HV/LV | weight % | 50/50 | 25/75 | | | |
| | mean particle size | µm | 1.2 | 1.1 | 1.6 | | |
| | Mw | g/mol | 195 900 | 199 100 | 195 200 | 217 000 | 214 000 |
| | Mn | g/mol | 78 380 | 79 850 | 77 810 | 70 000 | 69 700 |
| | Mw/Mn | | 2.5 | 2.5 | 2.5 | 3.1 | 3.1 |
| | Residue content | % by weight | 22.3 | 22.1 | 25.2 | 16.5 | 18.5 |
| | Swelling index | | 14.6 | 12.6 | 14.9 | 10.6 | 10.2 |
| | Melt index | g/10 min | 4 | 3.7 | 3.3 | 3.5 | 3.3 |
| | 1 kg Vicat point | °C. | 96.3 | 96.5 | 97 | | |
| Mechanical properties | notched Izod impact strength | kg cm/cm ² | 11.5 | 12.2 | 10.2 | 7.6 | 6.7 |
| | Flexural modulus | MPa | 1860 | 1990 | 1620 | | |
| | Tensile strength | MPa | 21 | 21 | 11 | 27.4 | 27.6 |
| | Flexural strength | MPa | 96 | 38 | | | |
| | | | | | | | |
| | | | | | | | |

TABLE 2

| UNIT | | | EXAMPLE 6 (comparative) | EXAMPLE 7 (comparative) | EXAMPLE 8 | EXAMPLE 9 | EXAMPLE 10 |
|---------------------------------------|-----------------------|----------|----------------------------|----------------------------|-----------|-----------|------------|
| Structure of the polymer compositions | Polybutadiene content | weight % | 8.1 | 8.3 | 8.3 | 8.2 | 6.1 |
| | HV/LV | weight % | 100/0 | 0/100 | 10/90 | 70/30 | 50/50 |
| | mean particle size | µm | 2.2 | 0.45 | 0.75 | 1.9 | 1.2 |
| | Mw | g/mol | | | | | |
| | Mn | g/mol | | | | | |
| | Mw/Mn | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
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TABLE 2-continued

| | UNIT | EXAMPLE 6 (comparative) | EXAMPLE 7 (comparative) | EXAMPLE 8 | EXAMPLE 9 | EXAMPLE 10 |
|-----------------------|-------------------|----------------------------|----------------------------|-----------|-----------|------------|
| | Residue content | | | | | |
| | Swelling index | | | | | |
| Mechanical properties | Melt index | 4.2 | 3.2 | 3.5 | 3.9 | 3.6 |
| | 1 kg Vicat | 96.5 | 96.8 | 97 | 96.4 | 95 |
| | point | | | | | |
| | notched Izod | 8.5 | 6.3 | 7.9 | 10.5 | 7.1 |
| | impact | | | | | |
| | strength | | | | | |
| | Flexural modulus | 1650 | 2100 | 1950 | 1930 | 2100 |
| | Tensile strength | 15 | 24 | 20 | 22 | 28.5 |
| | Flexural strength | | | | | |
| | MPa | | | | | |

We claim:

1. Polymer composition comprising a vinylaromatic polymer and a rubber containing polybutadiene, wherein the rubber is derived from a high-viscosity polybutadiene and from a low-viscosity polybutadiene, the said high-viscosity polybutadiene exhibiting a linear structure, a cis-1,4 structure content higher than 80% and a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 120 to 350 centipoises, and the said low-viscosity polybutadiene exhibiting a cis-1,4 structure content lower than 80% and a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 30 to 90 centipoises.

2. Composition according to claim 1, wherein the high-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 180 and 300 centipoises.

3. Composition according to claim 1, wherein the low-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 40 and 75 centipoises.

4. Composition according to claim 1, wherein the high-viscosity polybutadiene exhibits a cis-1,4 structure content higher than 90%.

5. Composition according to claim 1, wherein the low-viscosity polybutadiene exhibits a cis-1,4 structure content ranging from 30 to 60%.

6. Composition according to claim 1, wherein the high-viscosity polybutadiene exhibits a 1,2-vinyl structure content.

7. Composition according to claim 1, wherein the low-viscosity polybutadiene exhibits a 1,2-vinyl structure content.

8. Composition according to claim 1, wherein the high-viscosity polybutadiene represents 10 to 90% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 10% by weight of the total polybutadiene introduced.

9. Composition according to claim 8, wherein the high-viscosity polybutadiene represents 10 to 70% by weight of total polybutadiene introduced and in that the low-density polybutadiene represents 90 to 30% by weight of the total polybutadiene introduced.

10. Composition according to claim 1, wherein it contains 2 to 25% by weight of polybutadiene.

11. Composition according to claim 1, wherein the vinylaromatic polymer is polystyrene.

12. Composition according to claim 1, wherein it contains at least one plasticizer.

13. Composition according to claims 1, to 12, wherein it contains at least one antioxidant.

14. Process for the manufacture of a polymer composition comprising a vinylaromatic polymer and a rubber, comprising a stage of polymerization of at least one vinylaromatic monomer in the presence of a high-viscosity polybutadiene and of a low-viscosity polybutadiene and optionally of an organic solvent, wherein the high-viscosity polybutadiene exhibits a linear structure, a cis-1,4 structure content higher than 80% and a viscosity, measured at 25° C. at a concentration of 5% in styrene, ranging from 120 to 350 centipoises, and the low-viscosity polybutadiene exhibits a cis-1,4 structure content lower than 80% and a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 30 to 90 centipoises.

15. Process according to claim 14, wherein the high-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 180 and 300 centipoises.

16. Process according to claim 14, wherein the low-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 40 and 75 centipoises.

17. Process according to claim 14, wherein the high-viscosity polybutadiene exhibits a cis-1,4 structure content higher than 90%.

18. Process according to claim 14, wherein the low-viscosity polybutadiene exhibits a cis-1,4 structure content ranging from 30 to 60%.

19. Process according to claim 14, wherein the high-viscosity polybutadiene represents 10 to 90% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 10% by weight of the total polybutadiene introduced.

20. Process according to claim 19, wherein the high-viscosity polybutadiene represents 10 to 70% by weight of the total polybutadiene introduced and in that the low-density polybutadiene represents 90 to 30% by weight of the total polybutadiene introduced.

21. Process according to claim 14, wherein the polymerization stage is carried out in bulk.

22. Process according to claim 14, wherein at least one vinylaromatic monomer is styrene.

23. Process according to claim 14, characterized in that the polymerization stage is carried out in the presence of at least one adjuvant selected from the group consisting of plasticizers and antioxidants.

24. The composition according to claim 6 wherein the high viscosity polybutadiene exhibits a 1,2-vinyl structure content ranging from 0.1 to 5%.

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25. The composition according to claim 6 wherein the high viscosity polybutadiene exhibits a 1,2-vinyl structure content ranging from 0.5 to 3%.

26. The composition according to claim 7, characterized in that the low-viscosity polybutadiene exhibits a 1,2-vinyl structure content from 1 to 25%.

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27. The composition according to claim 7, characterized in that the low-viscosity polybutadiene exhibits a 1,2-vinyl structure content from 5 to 18%.

* * * * *

EXHIBIT 7



US005708081A

United States Patent [19]

Sarraf et al.

[11] **Patent Number:** 5,708,081[45] **Date of Patent:** Jan. 13, 1998

[54] **COMPOSITION COMPRISING A VINYLAROMATIC POLYMER AND A RUBBER AND PROCESS FOR OBTAINING IT**

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[52] **U.S. Cl.** 525/87; 525/316

[58] **Field of Search** 525/87, 316, 89, 525/98, 99

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[57] **ABSTRACT**

The invention relates to polymer compositions of high impact strength, comprising a vinylaromatic polymer and a rubber, and to a process for their manufacture.

These compositions are obtained by virtue of the use of two polybutadienes whose viscosities, measured at 25° C. at a concentration of 5% in styrene, are, respectively, between 120 and 350 centipoises in the case of one and between 30 and 90 centipoises in the case of the other.

27 Claims, No Drawings

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COMPOSITION COMPRISING A
VINYLAROMATIC POLYMER AND A
RUBBER AND PROCESS FOR OBTAINING
IT

TECHNICAL FIELD

The invention relates to polymer compositions comprising a vinylaromatic polymer and a rubber. These compositions are easy to process and exhibit good gloss and excellent mechanical properties.

They find applications in fields as diverse as electrical household appliances, that of office equipment or packaging.

PRIOR ART

Various techniques for improving the impact strength of compositions based on vinylaromatic polymer and rubber have been proposed.

Document EP 418,042 teaches an impact polystyrene composition comprising a branched polybutadiene exhibiting a double distribution of molecular masses, the ratio of the mean molecular masses of the component of high masses to that of low masses being higher than a factor of 2.5 and preferably between 3 and 5. The component of high molecular masses corresponds to branched molecules, while the component of low molecular masses corresponds to incompletely branched molecules. The polybutadiene has a cis-1,4 structure content which is preferably lower than 70% and more preferably lower than 50%.

The impact polystyrenes thus obtained have a marked bimodal structure and the distribution of their particle diameters indicates the presence of three distinct particle populations.

Document JP 4-100810 teaches the use of a mixture of two polybutadienes exhibiting very different viscosities. One of these polybutadienes must exhibit an intrinsic viscosity of between 3 and 7 dl/g, whereas the other polybutadiene must exhibit an intrinsic viscosity of between 0.5 and 1.4 dl/g. The use of such polybutadienes exhibits limits. In fact, the manufacture of a polybutadiene whose intrinsic viscosity is close to 7 dl/g is difficult to carry out. In addition, if the viscosity of the second polybutadiene is close to 1.4 dl/g, the viscosity of the polymer solution, which also contains the first polybutadiene of particularly high viscosity, becomes too high.

DESCRIPTION OF THE INVENTION

Polymer compositions comprising a vinylaromatic polymer and a rubber have now been found, the said rubber being derived from a high-viscosity polybutadiene and from a low-viscosity polybutadiene, the intrinsic viscosities of these two polybutadienes being close but different and such that that of the high-viscosity polybutadiene is lower than 3 dl/g and that of the low-viscosity polybutadiene is higher than 1.4 dl/g. The term rubber denotes the elastomeric phase present in the composition according to the invention.

This elastomeric phase contains all the mass of the polybutadienes initially introduced. The rubber of the compositions according to the invention therefore contains polybutadiene which may be partially crosslinked or grafted onto the vinylaromatic polymer. This rubber forms the shell of particles containing a proportion of the vinylaromatic polymer, the said particles themselves being dispersed in a matrix of vinylaromatic polymer.

The use of the two polybutadienes, of high and low viscosity, produces polymer compositions with remarkable

mechanical properties, in particular with regard to the impact strength. These properties are generally superior to those obtained by employing only one of these polybutadienes, with an appreciably identical polybutadiene content and with an appreciably identical degree of grafting of the polybutadiene with the vinylaromatic polymer in the polymer compositions being considered.

Furthermore, a polymer composition according to the invention exhibits an impact strength which is higher than the arithmetic mean of the impact strengths of the compositions obtained, on the one hand, with the high-viscosity polybutadiene by itself and, on the other hand, with the low-viscosity polybutadiene by itself, this being at a polybutadiene content which is appreciably identical and with an appreciably identical degree of grafting of polybutadiene with vinylaromatic polymer in the polymer compositions being considered.

This is reflected in the fact that if

P denotes the impact strength of a composition C according to the invention, in which the rubber is derived from a high-viscosity polybutadiene X and from a low-viscosity polybutadiene Y, x denoting the percentage by weight of X relative to the total weight of polybutadiene introduced and y denoting the percentage by weight of Y relative to the total weight of polybutadiene introduced,

P_x denotes the impact strength of a composition C_x comprising the same vinylaromatic polymer as C and a rubber obtained exclusively from X, the polybutadiene content in C_x being here identical with the polybutadiene content in C, the degrees of grafting of the polybutadienes in C and C_x being appreciably identical,

P_y denotes the impact strength of a composition C_y comprising the same vinylaromatic polymer as C and a rubber obtained exclusively from Y, the polybutadiene content in C_y being here identical with the polybutadiene content in C, the degree of grafting of the polybutadienes in C and C_y being appreciably identical,

there is a relationship P>

$$\frac{xP_x + yP_y}{x + y}$$

In addition, a composition according to the invention generally exhibits mechanical properties which are superior to those obtained by the use of a single polybutadiene whose viscosity is comparable with the viscosity of a mixture of the polybutadienes employed for producing the said composition, the said mixture containing the high- and low-viscosity polybutadienes in proportions which are identical with those employed for the production of the composition according to the invention, the degrees of grafting of the polybutadienes in the polymer compositions being considered being appreciably identical.

This last comparison with a single polybutadiene is meaningful only if the latter itself is not a mixture of different polybutadienes and, in any event, exhibits a polydispersity, that is to say a ratio of its mass-average molecular mass to its number-average molecular mass, lower than 4.

The high-viscosity polybutadiene is of linear structure, has a cis-1,4 structure content higher than 80% and preferably higher than 90% and exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 120 to 350 centipoises and preferably from 180 to 300

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centipoises. The low-viscosity polybutadiene is of linear, branched or star-shaped structure, has a cis-1,4 structure content lower than 80% and preferably between 30 and 60% and exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 30 to 90 centipoises and preferably from 40 to 75 centipoises.

The high-viscosity polybutadiene preferably exhibits a 1,2-vinyl structure content ranging from 0.1 to 5% and more preferably from 0.5 to 3%.

The low-viscosity polybutadiene preferably exhibits a 1,2-vinyl structure content ranging from 1 to 25% and more preferably from 5 to 18%.

The use of the polybutadienes described above is preferably carried out so that the high-viscosity polybutadiene represents 10 to 90% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 10% by weight of the total polybutadiene introduced.

Preferably, also, the use of the polybutadienes described above is carried out so that the high-viscosity polybutadiene represents 10 to 70% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 30% by weight of the total butadiene introduced.

The compositions according to the invention preferably contain polybutadiene in a proportion of 2 to 25%. This includes all the polybutadiene present in the compositions, either in a partially crosslinked form or in a form grafted onto the vinylaromatic polymer, the grafted vinylaromatic polymer itself not being included in the percentage of polybutadiene shown above.

The vinylaromatic polymer is obtained by the polymerization of at least one vinylaromatic monomer described below. It may therefore be a copolymer.

It is not ruled out that the polymer composition may contain the adjuvants which are usual in vinylaromatic polymers, such as at least one antioxidant and/or at least one plasticizer.

Another subject of the invention relates to a process for the manufacture of the polymer compositions described above.

The process according to the invention, which can function continuously or noncontinuously, comprises a stage of polymerization of at least one vinylaromatic monomer in the presence of high- and low-viscosity polybutadienes described above.

This polymerization stage maybe a suspension or bulk polymerization process, the principle of these two techniques being well known to a person skilled in the art. In the case of the polymerization must take place in bulk the polybutadienes are first of all dissolved in at least one vinylaromatic monomer, optionally in the presence of an organic solvent, and a polymerization is then carried out, the initiation of which may be thermal or using peroxide. If its initiation is thermal, this polymerization may be conducted between 110° and 180° C. and preferably between 120° and 160° C. If the initiation of the polymerization uses peroxide, the polymerization will be generally conducted between 70° and 180° C. and preferably between 90° and 160° C. During this polymerization stage the vinylaromatic monomer is polymerized either by itself or with a proportion of the polybutadienes and in this latter case grafting is said to take place between the polybutadienes and the vinylaromatic monomer and, in addition, the polybutadienes are partially crosslinked.

During these reactions the well-known phenomenon of phase inversion takes place, resulting in the formation of particles dispersed in vinylaromatic polymer.

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The stirring must be sufficient for this dispersion of particles to be uniform.

Following the polymerization stage it is appropriate to proceed to the removal of the volatile species such as unreacted monomers and possibly solvent. This may be carried out using conventional techniques such as by the use of a devolatilizer operating with heating and under vacuum.

The final polybutadiene and vinylaromatic polymer content of the composition according to the invention depends on the degree of progress of the polymerization carried out before removal of the volatile species. In fact, if the degree of progress of polymerization is low, the removal of the volatile species will result in the removal of a large quantity of vinylaromatic monomer and the final polybutadiene content of the composition will be higher. In order not to produce an excessively high crosslinking of the polybutadienes it is preferable not to force the polymerization of the vinylaromatic monomers to 100%.

The progress of the polymerization can be followed by virtue of samples taken during the polymerization stage and by determining the solids content on the samples withdrawn. The solids content means the percentage by weight of solid obtained after evaporation of the withdrawn samples in a vacuum of 25 mbar for approximately 20 minutes at 200° C., in relation to the initial weight of the sample. This treatment removes from the withdrawn sample the vinylaromatic monomers unpolymersed at the time of the withdrawal. The polymerization can be taken further, for example until a solids content of 70 or 80% is obtained.

At least one adjuvant or polymerization initiator, these being conventional in this kind of preparation, may be added to the polymerization mixture before or during the polymerization. These adjuvants may be plasticizers such as mineral oils, butyl stearate or dioctyl phthalate, stabilizers such as antioxidants, which may be phenol substituted by an alkyl group, such as di-tert-butyl-para-cresol, or phosphites such as trionyl phenylphosphite.

A plasticizing oil may be introduced, generally in a proportion such that it is present in the final composition in a ratio of 0 to 8% by weight and preferably in a ratio of 0 to 5% by weight.

The polymerization initiators which are optionally added are those usually employed for this kind of preparation. They may be chosen from peroxides such as dibenzoyl peroxide, tert-butyl peroxybenzoate and 1,1-bis(tert-butylperoxy)cyclohexane.

Vinylaromatic monomer is intended to mean styrene, styrene substituted by an alkyl group on the vinyl group, such as alpha-methylstyrene or alpha-ethylstyrene, styrene substituted by an alkyl group on the ring, such as ortho-vinyltoluene, para-vinyltoluene, ortho-ethylstyrene or 2,4-dimethylstyrene, styrene substituted by a halogen on the ring, such as, for example, 2,4-dichlorostyrene, and styrene substituted both by a halogen and an alkyl group, such as 2-chloro-4-methylstyrene, as well as vinylanthracene. Styrene is a preferred vinylaromatic monomer.

The polymerization may be conducted in the presence of an organic solvent. This solvent will be chosen so that it does not boil under polymerization conditions and so that it is miscible with the vinylaromatic monomer and the vinylaromatic polymer derived therefrom. It is possible to employ alicyclic hydrocarbons such as cyclohexane or, preferably, aromatics such as toluene, benzene, ethylbenzene or xylene.

In general, the quantity of solvent which is employed will be such that the polymerization mixture does not contain more than 40% by weight of organic solvent.

EMBODIMENTS OF THE INVENTION

In the examples which follow, the structure and the properties of the polymer compositions obtained have been determined by the following techniques:

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melt flow index: ISO standard 1133 condition H
 1-kg Vicat point: ISO standard 306 A
 notched Izod impact strength: ISO standard 180/1A
 elasticity modulus measured in flexure: ISO standard 178
 tensile and flexural strength: ISO standard R527
 molecular mass of the polystyrene: the polystyrene is
 extracted from the impact polystyrene using methyl
 ethyl ketone and its molecular mass is measured by gel
 permeation chromatography (GPC).

In Table 1 Mw denotes the weight-average molecular
 mass of the polystyrene, Mn denotes the number-average
 molecular mass of the polystyrene and Mw/Mn denotes the
 ratio of the weight-average molecular mass to the number-
 average molecular mass of the polystyrene.

swelling ratio and residue content 0.4 grams of impact
 polystyrene are placed in 40 ml of toluene at ambient
 temperature with stirring for two hours. The composi-
 tion thus obtained is then centrifuged at 20,000 revo-
 lutions per minute for 30 minutes so as to make it
 possible to separate off the gel formed from the solu-
 tion. The wet (toluene-impregnated) gel obtained after
 separation from the solution is then dried in vacuum at
 80° C. and a dry gel is obtained.

If Mh denotes the mass of wet gel, Md the mass of dry gel
 and Mt the mass of the impact polystyrene test sample, the
 swelling index SI is given by the formula $SI = Mh/Md$ and the
 residue content Cr, expressed as percentage by weight, is
 given by the formula $Cr = Md/Mt \times 100$.

The residue content indicates approximately the rubber
 content of the polymer composition since it adds the total
 percentage by weight of polybutadiene and the percentage
 by weight of polystyrene grafted to polybutadiene in the
 polymer composition.

Two compositions exhibiting an identical residue content
 and an identical polybutadiene content will therefore be
 considered as exhibiting an identical degree of grafting
 between the polybutadiene and the polystyrene.

polybutadiene content in the compositions: NF standard T
 51-007

mean size of the rubber particles: by sedimentation par-
 ticle size determination (capa 700) after dissolving in
 methyl ethyl ketone.

In the tables, the line "HV/LV" gives the relative percent-
 age by weight of high-viscosity polybutadiene ("HV") and
 of low-viscosity polybutadiene ("LV").

EXAMPLE 1

Into a 15-litre reactor fitted with a mechanical stirrer and
 a temperature control are introduced 7.9 kg of styrene, 1.2
 kg of ethylbenzene and 300 grams of a plasticizing oil with
 a viscosity of 210 centipoises at 20° C., of Primol 352
 trademark, marketed by Esso.

300 grams of a first polybutadiene of trademark BR 1202
 G, marketed by Shell, are then introduced at ambient tem-
 perature and with stirring in the form of gummy solid pieces,
 the said polybutadiene being of linear structure and exhib-
 iting a viscosity of 160 centipoises at 25° C. at a concen-
 tration of 5% in styrene and an intrinsic viscosity of 2.5 dl/g
 at 25° C., a weight-average molecular mass of 287 000, a
 cis-1,4 structure content of 96.5, followed by 300 grams of
 a second polybutadiene of trademark P 1001, marketed by
 Enichem, in the form of gummy solid pieces, the said
 polybutadiene being of branched structure and exhibiting a
 viscosity of 45 centipoises at 25° C. at a concentration of 5%
 in styrene and an intrinsic viscosity of 1.9 dl/g at 25° C., a

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weight-average molecular mass of 175 000, a cis-1,4 struc-
 ture content of 45% and a 1,2-vinyl structure content of
 11%.

The two polybutadienes were therefore introduced into
 the reactor in equal quantity. By way of guidance it is
 mentioned that an equal parts mixture of these two polyb-
 utadienes exhibits a viscosity of 120 centipoises at 25° C. at
 a concentration of 5% in styrene.

After the polybutadiene has dissolved completely, thermal
 polymerization of the solution is started. The progress of the
 polymerization is followed by measuring the solids content
 obtained from withdrawals taken during the polymerization.
 The solids content corresponds to the percentage by weight
 of solid obtained after vacuum evaporation at 200° C. of the
 samples withdrawn, relative to the initial weight of the
 sample.

The reactor is first of all heated to 126° C. until a solids
 content of 27% is obtained. The temperature is then raised
 from 126° to 157° C. over 90 minutes. The solids content at
 this time is approximately 70%. The content of the reactor
 is then transferred to a devolatilizer at approximately 180°
 C. under vacuum, for approximately 10 minutes so as to
 extract the unpolymerized styrene and the ethylbenzene. The
 product obtained is granulated in a manner which is known
 to a Person skilled in the art. Specimens are produced by
 injection moulding for carrying out the mechanical tests.
 The results are collated in Table 1. The impact polystyrene
 obtained exhibits a monomodal particle size distribution
 with a maximum at about 1 µm.

EXAMPLE 2

Example 1 is repeated, except that 150 grams of the first
 polybutadiene and 450 grams of the second polybutadiene
 are introduced. The results are collated in Table 1.

EXAMPLE 3 (Comparative)

Example 1 is repeated, except that the 300 grams of the
 first polybutadiene and the 300 grams of the second polyb-
 utadiene are replaced with 600 grams of a linear polybuta-
 diene of trademark HX 529C, marketed by Bayer, with a
 viscosity of 140 centipoises at 25° C. at a concentration of
 5% in styrene and intrinsic viscosity of 2.1 dl/g at 25° C.,
 with a weight-average molecular mass of 224 000, polydis-
 persity of 1.26, cis-1,4 structure content of 38% and 1,2-
 vinyl structure content of 11%. The results are collated in
 Table 1.

EXAMPLE 4

Into a 15-litre reactor fitted with a mechanical stirrer and
 a temperature control are introduced 9 kg of styrene, 0.6 kg
 of ethylbenzene, 0.2 kg of a plasticizing oil with a viscosity
 of 210 centipoises at 20° C., of Primol 352 trademark,
 marketed by Esso.

200 grams of a first polybutadiene of trademark BR
 1202G, marketed by Shell, are then introduced at ambient
 temperature and with stirring in the form of gummy solid
 pieces, the said polybutadiene being of linear structure and
 exhibiting a viscosity of 160 centipoises at 25° C. at a
 concentration of 5% in styrene and an intrinsic viscosity of
 2.5 dl/g at 25° C., a weight-average molecular mass of 287
 000, a cis-1,4 structure content of 96.5%, followed by 200
 grams of a second polybutadiene of trademark HX 565SIC,
 marketed by Bayer, in the form of gummy solid pieces, said
 polybutadiene being of branched structure and exhibiting a
 viscosity of 40 centipoises at 25° C. at a concentration of 5%

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in styrene and an intrinsic viscosity of 1.7 dl/g at 25° C., a weight-average molecular mass of 165 000, a cis-1,4 structure content of 37% and a 1,2-vinyl structure content of 11%.

After the polybutadiene has dissolved completely, thermal polymerization of the solution is started in a way identical with the polymerization procedure described in Example 1. The results are collated in Table 1.

EXAMPLE 5 (comparative)

The procedure is as in Example 4, except that the 200 grams of the second polybutadiene are replaced with 200 grams of a linear polybutadiene of trademark H 529C marketed by Bayer, exhibiting a viscosity of 120 centipoises at 25° C. at a concentration of 5% in styrene and an intrinsic viscosity of 2.1 dl/g at 25° C., a weight-average molecular mass of 224 000, a cis-1,4 structure content of 38% and a 1,2-vinyl structure content of 11%. The results are collated in Table 1.

EXAMPLE 6 (comparative)

The procedure is as in Example 1, except that 600 grams of the first polybutadiene are introduced and no second polybutadiene.

The results are collated in Table 2.

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EXAMPLE 7 (comparative)

The procedure is as in Example 1, except that 600 grams of the second polybutadiene are introduced and no first polybutadiene.

The results are collated in Table 2.

EXAMPLE 8

The procedure is as in Example 1, except that 60 grams of the first polybutadiene and 540 grams of the second polybutadiene are introduced.

The results are collated in Table 2.

EXAMPLE 9

The procedure is as in Example 1, except that 420 grams of the first polybutadiene and 180 grams of the second polybutadiene are introduced.

The results are collated in Table 2.

EXAMPLE 10

The procedure is as in Example 4, except that the 200 grams of polybutadiene of trademark BR 1202 G are replaced with 200 grams of a polybutadiene of trademark BR 40 marketed by Enichem, the latter polybutadiene having a cis-1,4 structure content higher than 98% and a viscosity of 330 centipoises at 25° C. at a concentration of 5% in styrene.

The results are collated in Table 2.

TABLE 1

| UNIT | | | EXAMPLE 1 | EXAMPLE 2 | EXAMPLE 3 (comparative) | EXAMPLE 4 | EXAMPLE 5 (comparative) |
|---------------------------------------|------------------------------|-----------------------|-----------|-----------|----------------------------|-----------|----------------------------|
| Structure of the polymer compositions | Polybutadiene content | weight % | 8.2 | 8.5 | 8.4 | 6.3 | 6.1 |
| | HV/LV | weight % | 50/50 | 25/75 | | | |
| | mean particle size | µm | 1.2 | 1.1 | 1.6 | | |
| | Mw | g/mol | 195 900 | 199 100 | 195 200 | 217 000 | 214 000 |
| | Mn | g/mol | 78 380 | 79 850 | 77 810 | 70 000 | 69 700 |
| Mechanical properties | Mw/Mn | | 2.5 | 2.5 | 2.5 | 3.1 | 3.1 |
| | Residue content | % by weight | 22.3 | 22.1 | 25.2 | 16.5 | 18.5 |
| | Swelling index | | 14.6 | 12.6 | 14.9 | 10.6 | 10.2 |
| | Melt index | g/10 min | 4 | 3.7 | 3.3 | 3.5 | 3.3 |
| | 1 kg Vicat point | °C. | 96.3 | 96.5 | 97 | | |
| | notched Izod impact strength | kg cm/cm ² | 11.5 | 12.2 | 10.2 | 7.6 | 6.7 |
| | Flexural modulus | MPa | 1860 | 1990 | 1620 | | |
| | Tensile strength | MPa | 21 | 21 | 11 | 27.4 | 27.6 |
| | Flexural strength | MPa | 36 | 38 | | | |
| | | | | | | | |

TABLE 2

| UNIT | | | EXAMPLE 6 (comparative) | EXAMPLE 7 (comparative) | EXAMPLE 8 | EXAMPLE 9 | EXAMPLE 10 |
|---------------------------------------|-----------------------|----------|----------------------------|----------------------------|-----------|-----------|------------|
| Structure of the polymer compositions | Polybutadiene content | weight % | 8.1 | 8.3 | 8.3 | 8.2 | 6.1 |
| | HV/LV | weight % | 100/0 | 0/100 | 10/90 | 70/30 | 50/50 |
| | mean particle size | µm | 2.2 | 0.45 | 0.75 | 1.9 | 1.2 |
| | Mw | g/mol | | | | | |
| | Mn | g/mol | | | | | |
| | Mw/Mn | | | | | | |
| | | | | | | | |

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TABLE 2-continued

| | UNIT | EXAMPLE 6 (comparative) | EXAMPLE 7 (comparative) | EXAMPLE 8 | EXAMPLE 9 | EXAMPLE 10 |
|------------|--------------------|----------------------------|----------------------------|-----------|-----------|------------|
| | Residue content | | | | | |
| | Swelling index | | | | | |
| Mechanical | Melt index | 4.2 | 3.2 | 3.5 | 3.9 | 3.6 |
| properties | 1 kg Vicat | 96.5 | 96.8 | 97 | 96.4 | 95 |
| | point | | | | | |
| | notched Izod | 8.5 | 6.3 | 7.9 | 10.5 | 7.1 |
| | impact | | | | | |
| | strength | | | | | |
| | Flexural | 1650 | 2100 | 1990 | 1930 | 2100 |
| | modulus | | | | | |
| | Tensile | 15 | 24 | 20 | 22 | 28.5 |
| | strength | | | | | |
| | Flexural | | | | | |
| | strength | | | | | |

We claim:

1. Polymer composition comprising a vinylaromatic polymer and a rubber containing polybutadiene, wherein the rubber is derived from a high-viscosity polybutadiene and from a low-viscosity polybutadiene, the said high-viscosity polybutadiene exhibiting a linear structure, a cis-1,4 structure content higher than 80% and a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 120 to 350 centipoises, and the said low-viscosity polybutadiene exhibiting a cis-1,4 structure content lower than 80% and a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 30 to 90 centipoises.

2. Composition according to claim 1, wherein the high-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 180 and 300 centipoises.

3. Composition according to claim 1, wherein the low-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 40 and 75 centipoises.

4. Composition according to claim 1, wherein the high-viscosity polybutadiene exhibits a cis-1,4 structure content higher than 90%.

5. Composition according to claim 1, wherein the low-viscosity polybutadiene exhibits a cis-1,4 structure content ranging from 30 to 60%.

6. Composition according to claim 1, wherein the high-viscosity polybutadiene exhibits a 1,2-vinyl structure content.

7. Composition according to claim 1, wherein the low-viscosity polybutadiene exhibits a 1,2-vinyl structure content.

8. Composition according to claim 1, wherein the high-viscosity polybutadiene represents 10 to 90% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 10% by weight of the total polybutadiene introduced.

9. Composition according to claim 8, wherein the high-viscosity polybutadiene represents 10 to 70% by weight of total polybutadiene introduced and in that the low-density polybutadiene represents 90 to 30% by weight of the total polybutadiene introduced.

10. Composition according to claim 1, wherein it contains 2 to 25% by weight of polybutadiene.

11. Composition according to claim 1, wherein the vinylaromatic polymer is polystyrene.

12. Composition according to claim 1, wherein it contains at least one plasticizer.

13. Composition according to claims 1, to 12, wherein it contains at least one antioxidant.

14. Process for the manufacture of a polymer composition comprising a vinylaromatic polymer and a rubber, comprising a stage of polymerization of at least one vinylaromatic monomer in the presence of a high-viscosity polybutadiene and of a low-viscosity polybutadiene and optionally of an organic solvent, wherein the high-viscosity polybutadiene exhibits a linear structure, a cis-1,4 structure content higher than 80% and a viscosity, measured at 25° C. at a concentration of 5% in styrene, ranging from 120 to 350 centipoises, and the low-viscosity polybutadiene exhibits a cis-1,4 structure content lower than 80% and a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, ranging from 30 to 90 centipoises.

15. Process according to claim 14, wherein the high-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 180 and 300 centipoises.

16. Process according to claim 14, wherein the low-viscosity polybutadiene exhibits a viscosity, measured at 25° C. at a concentration of 5% by weight in styrene, of between 40 and 75 centipoises.

17. Process according to claim 14, wherein the high-viscosity polybutadiene exhibits a cis-1,4 structure content higher than 90%.

18. Process according to claim 14, wherein the low-viscosity polybutadiene exhibits a cis-1,4 structure content ranging from 30 to 60%.

19. Process according to claim 14, wherein the high-viscosity polybutadiene represents 10 to 90% by weight of the total polybutadiene introduced and in that the low-viscosity polybutadiene represents 90 to 10% by weight of the total polybutadiene introduced.

20. Process according to claim 19, wherein the high-viscosity polybutadiene represents 10 to 70% by weight of the total polybutadiene introduced and in that the low-density polybutadiene represents 90 to 30% by weight of the total polybutadiene introduced.

21. Process according to claim 14, wherein the polymerization stage is carried out in bulk.

22. Process according to claim 14, wherein at least one vinylaromatic monomer is styrene.

23. Process according to claim 14, characterized in that the polymerization stage is carried out in the presence of at least one adjuvant selected from the group consisting of plasticizers and antioxidants.

24. The composition according to claim 6 wherein the high viscosity polybutadiene exhibits a 1,2-vinyl structure content ranging from 0.1 to 5%.

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25. The composition according to claim 6 wherein the high viscosity polybutadiene exhibits a 1,2-vinyl structure content ranging from 0.5 to 3%.

26. The composition according to claim 7, characterized in that the low-viscosity polybutadiene exhibits a 1,2-vinyl structure content from 1 to 25%.

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27. The composition according to claim 7, characterized in that the low-viscosity polybutadiene exhibits a 1,2-vinyl structure content from 5 to 18%.

* * * * *

EXHIBIT 8

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT 9

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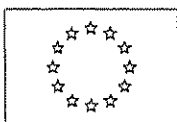
***Case No COMP/M.2354 -
ENICHEM / POLIMERI***

Only the English text is available and authentic.

**REGULATION (EEC) No 4064/89
MERGER PROCEDURE**

Article 6(1)(b) NON-OPPOSITION
Date: 06/04/2001

*Also available in the CELEX database
Document No 301M2354*



COMMISSION OF THE EUROPEAN COMMUNITIES

Brussels, 06/04/2001
SG (2001) D/ 287581

MERGER PROCEDURE
ARTICLE 6(1)(b) DECISION

SIMPLIFIED PROCEDURE

PUBLIC VERSION

To the notifying party:

Subject: Case No. COMP/M.2354 - ENICHEM / POLIMERI
Notification of 8.03.2001 pursuant to Article 4 of Council Regulation (EEC) No. 4064/89¹
Publication in the Official Journal of the European Communities No. C 86/4 of 16/03/2001

1. On 8.03.2001 the Commission received a notification of a proposed concentration pursuant to Article 4 of Council Regulation (EEC) No 4064/89 by which the Italian company, EniChem S.p.A. ("EniChem"), belonging to the ENI Group, acquires within the meaning of Article 3(1)(b) of the Council Regulation, by way of an exchange of businesses, sole control of the whole of the Italian company, Polimeri Europe S.r.l. ("Polimeri"), which it has jointly-controlled up to the present with the Dow Chemical Company ("DOW") as a 50:50 joint venture.

The business activities of the undertakings concerned are :

- EniChem : development, production and sale of chemicals products;
- Polimeri : production and sale of polyethylene resins.

¹ OJ L 395, 30.12.1989 p. 1; corrected version OJ L 257 of 21.9.1990, p. 13, as last amended by Regulation (EC) No 1310/97, OJ L 180, 9.7.1997, p. 1, corrigendum in OJ L 40, 13.2.1998, p. 17.

2. After examination of the notification, the Commission has concluded that the notified operation falls within the scope of Council Regulation (EEC) No. 4064/89 and of paragraph 4,(c) of the Commission Notice on a simplified procedure for treatment of certain concentrations under Council Regulation (EEC) No 4064/89².
3. For the reasons set out in the Notice on a simplified procedure, the Commission has decided not to oppose the notified operation and to declare it compatible with the common market and with the EEA Agreement. This decision is adopted in application of Article 6(1)(b) of Council Regulation (EEC) No. 4064/89.

For the Commission,

(Signed)

M. MONTI

Member of the Commission

² OJ C 217, 29.07.2000, p. 32.

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EXHIBIT 10

United States Patent [19]**Sullivan**[11] **Patent Number:** **4,852,884**[45] **Date of Patent:** **Aug. 1, 1989**

- [54] **USE OF METAL CARBAMATE
ACCELERATOR IN PEROXIDE-CURED
GOLF BALL CENTER FORMULATION**
- [75] **Inventor:** Michael J. Sullivan, Chicopee, Mass.
- [73] **Assignee:** Spalding & Evenflo Companies, Inc.,
Tampa, Fla.
- [21] **Appl. No.:** 137,647
- [22] **Filed:** Dec. 24, 1987
- [51] **Int. Cl.⁴** A63B 37/06
- [52] **U.S. Cl.** 273/230; 273/DIG. 022;
273/235 R; 524/197; 524/202; 524/322;
524/432; 525/259; 525/261
- [58] **Field of Search** 524/908, 197, 198, 202,
524/322, 432; 273/218, 228, 230; 525/261, 259

[56] **References Cited****U.S. PATENT DOCUMENTS**

4,266,772 5/1981 Martin et al. 524/430
 4,483,537 1/1984 Hanada et al. 524/908
 4,561,857 12/1985 Tominaga et al. 524/908
 4,683,257 7/1987 Kakiuchi et al. 524/908

Primary Examiner—Allan M. Lieberman
Attorney, Agent, or Firm—Donald R. Bahr

[57] **ABSTRACT**

Golf balls exhibiting a satisfactory coefficient of restitution while having higher Riehle compression and hence a softer feel are provided by the inclusion of a metallic dithiocarbamate in the core formulation.

24 Claims, No Drawings

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USE OF METAL CARBAMATE ACCELERATOR IN PEROXIDE-CURED GOLF BALL CENTER FORMULATION

This invention relates to improved golf balls. More particularly, this invention relates to improved core compositions for use in producing unitary golf balls.

In the prior art, it has become rather standard practice throughout the golfing industry to provide golf balls of unitary construction, generally consisting of a cover produced from ionomeric resins and a center part or core of cross-linked polybutadiene or other elastomers. Golf balls produced with such unitary construction are taught in U.S. Pat. No. 3,313,545, issued Apr. 11, 1967; U.S. Pat. No. 3,438,933, issued Apr. 15, 1969; and U.S. Pat. No. 4,625,964 issued Dec. 2, 1986.

A number of distinct advantages exist in the employment of unitary construction techniques in producing golf balls, as contrasted to the wound golf balls of the earlier art. Unitary golf balls can be produced with an essentially perfect center of gravity and, thus, exhibit excellent aerodynamic properties, superior roll and trueness of flight. Such golf balls are highly resistant to cutting and are practically indestructible during normal play. The balls return to round even after severe distortion and maintain their superior flight characteristics after extended use. Further, homogeneous unitary golf balls may be manufactured with better quality than the conventional wound balls.

In contrast to the covered wound golf balls, unitary balls maintain their playing characteristics throughout widely varying temperature ranges, possess an excellent shelf life and will not water log. In those situations where the paint on unitary golf balls becomes worn or damaged, the balls may be readily reclaimed by removing or stripping off the old paint, followed by repainting. By contrast, conventional wound balls seldom last long enough to allow repainting.

While such unitary golf balls have found wide acceptance, the advantages gained in increased durability have been offset to a large degree by decreased playability.

It is an object of the present invention to provide unitary golf balls exhibiting superior playability while maintaining a satisfactory coefficient of restitution.

In accordance with the present invention, there is provided a unitary golf ball comprising a solid core and a cover therefor, the solid core comprising polybutadiene and mixtures thereof, at least one metallic salt of an unsaturated carboxylic acid, a source of free radicals and from about 0.1 to about 0.5 parts by weight, based on 100 parts elastomer, of a polyvalent metal adduct of dialkyl dithiocarbamate, and the cover comprising at least one layer of an ionomeric resin-based composition.

The core compositions of the present invention may be based on polybutadiene, and mixtures of polybutadiene with other elastomers. It is preferred that the base elastomer have a relatively high molecular weight. The broad range for the molecular weight of suitable base elastomers is from about 50,000 to about 500,000. A more preferred range for the molecular weight of the base elastomer is from about 100,000 to about 500,000. As a base elastomer for the core composition, cis-polybutadiene is preferably employed, or a blend of cis-polybutadiene with other elastomers may also be utilized. Most preferably, cis-polybutadiene having a

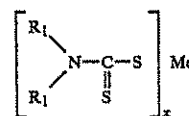
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weight-average molecular weight of from about 100,000 to about 500,000 is employed.

The unsaturated carboxylic acid component of the core composition is the reaction product of the carboxylic acid and an oxide or carbonate of a metal such as zinc, magnesium, barium, calcium, lithium, sodium, potassium, cadmium, lead, tin and the like, and mixtures thereof. Preferably, the oxides of polyvalent metals, i.e., those having a valence of at least 2, and more preferably, oxides of divalent metals such as zinc, magnesium and cadmium are employed. Most preferably, zinc oxide is utilized.

Examples of unsaturated carboxylic acids which find utility in producing the present core compositions are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid and the like, and mixtures thereof. Preferably, the carboxylic acid component is either acrylic or methacrylic acid. Usually, from about 20 to about 50, preferably from about 25 to about 35 parts by weight per 100 parts of elastomer, of the metal salt is included in the core composition.

The dithiocarbamate component of the core composition is selected from those compounds of the formula



wherein R_1 is lower alkyl containing from 1 to about 5 carbon atoms, Me is a metallic cation having a valence of from 2 to 4, and x is an integer having a value equal to the valence of the cation.

Exemplary of R_1 are methyl, ethyl and butyl. Exemplary of suitable cations are zinc, lead, cadmium, tellurium, copper, bismuth and selenium. Preferably, the cation used is zinc and the carbamates are zinc dimethyl dithiocarbamate (methyl zimate) ethyl or butyl zimate. Most preferably, the carbamate is zinc dimethyl dithiocarbamate. As previously indicated, the metallic dithiocarbamate is included in the core composition in an amount of from about 0.1 to about 0.5 parts by weight per 100 parts elastomer, preferably in an amount of from about 0.1 to about 0.4.

The free radical initiator included in the core composition is any conventionally known polymerization initiator which decomposes during the cure cycle. The amount of the selected initiator present is dictated only by the requirements of catalytic activity as a polymerization initiator. Suitable initiators for use in the present invention include peroxides, persulfates, azo compounds, hydrazines and the like. Peroxides such as dicumyl peroxide, n-butyl 4,4-bis (butylperoxy) valerate, 1,1-bis (t-butylperoxy)-3,3,5-trimethylcyclohexane, di-t-butylperoxide and 2,5-di-(t-butylperoxy)-2,5 dimethylhexane are readily commercially available and conveniently used, generally in amounts of from about 0.1 to about 10.0 and preferably in amount of from about 0.3 to about 3.0 parts by weight based on 100 parts elastomer.

The core compositions of the present invention may additionally contain any other suitable and compatible modifying ingredients including, but not limited to, fillers, metal oxides, fatty acids, and diisocyanates.

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As fillers, any known and conventional filler material, or mixtures thereof, may be used. Such fillers should be in finely divided form, as for example, in a size generally less than about 20 mesh and preferably less than about 100 mesh U.S. standard screen size. Suitable fillers include silica, silicates, zinc oxide, carbon black, cork, titania, cotton flock, cellulose flock, leather fiber, plastic and/or leather flour, asbestos, glass fibers, metal carbonates and talc. Particularly useful is the oxide or carbonate of the cation used in forming the metal salt of the unsaturated carboxylic acid component.

The amount of filler included in the core composition is primarily dictated by weight restrictions and is preferably from about 10 to about 100 parts by weight per 100 parts elastomer.

Fatty acids may also be included in the compositions, functioning to improve moldability and processing. Generally, fatty acids having from about 10 to about 40 carbon atoms are used, preferably those having from about 15 to about 20 atoms. Exemplary of suitable fatty acids are stearic acid and linoleic acid. When employed, the selected fatty acids, or mixtures thereof, are included in the core composition in amounts of from about 1 to about 15, more preferably in an amount of from about 2 to about 10, and most preferably in an amount of from about 2 to about 5 parts by weight based on 100 parts elastomer. It is preferred that the core compositions include stearic acid as the fatty acid adjunct in an amount of from about 2 to about 5 parts by weight based on 100 parts elastomer.

Diisocyanates may also be optionally included in the core compositions for the purpose of increasing the coefficient of restitution of resultant cores. When utilized, the diisocyanates are included in amounts of from about 0.2 to about 5.0 parts by weight based on 100 parts elastomer. Exemplary of a suitable diisocyanate is 4,4-diphenylmethane diisocyanate.

In producing golf ball cores utilizing the present compositions, the ingredients may be intimately mixed using, for example, two roll mills or a Banbury mixer until the composition is uniform, usually over a period of from about 5 to about 20 minutes. The sequence of addition of components is not critical. A preferred blending sequence is as follows.

Elastomer, filler, zinc salt, metal oxide, fatty acid and the metallic dithiocarbamate are blended for about 7 minutes in an internal mixer such as a Banbury mixer. As a result of shear during mixing the temperature rises to about 200° F. The initiator and diisocyanate are then added and the mixing continued until the temperature reaches about 220° F. whereupon the batch is discharged onto a two roll mill, mixed for about one minute and sheeted out.

The sheet is then placed in a Barwell preformer and slugs are produced. The slugs are then subjected to compression molding at about 320° F. for about 14 minutes. After molding and cooling, the cooling effected at room temperature for about 4 hours, the molded cores are subjected to a centerless grinding operation whereby a thin layer of the molded core is removed to produce a round core having a diameter of 1.545 inches.

The mixing is desirably conducted in such a manner that the composition does not reach incipient polymerization temperatures during the blending of the various components.

Usually the curable component of the composition will be cured by heating the composition at elevated

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temperatures on the order of from about 275° F. to about 350° F., preferably and usually from about 295° F. to about 325° F., with molding of the composition effected simultaneously with the curing thereof. The composition can be formed into a core structure by any one of a variety of molding techniques, e.g., injection, compression or transfer molding. When the composition is cured by heating, the time required for heating will normally be short, generally from about 10 to about 20 minutes, depending upon the particular curing agent used. Those of ordinary skill in the art relating to free radical curing agents for polymers are conversant with adjustments of cure times and temperatures required to effect optimum results with any specific free radical agent.

After molding, the core is removed from the mold and the surface thereof, preferably treated to facilitate adhesion thereof to the covering materials. Surface treatment can be effected by any of the several techniques known in the art, such as corona discharge, ozone treatment, sand blasting and the like. Preferably, surface treatment is effected by grinding with an abrasive wheel.

The core is converted into a golf ball by providing at least one layer of covering material thereon, ranging in thickness from about 0.050 to about 0.250 inch and preferably from about 0.060 to about 0.090 inch. The cover composition preferably is made from ethylene-acrylic acid or ethylene-methacrylic acid copolymers neutralized with mono or polyvalent metals such as sodium, potassium, lithium, calcium, zinc or magnesium.

The ionic copolymers used to produce the cover compositions may be made according to known procedures, such as those in U.S. Pat. No. 3,421,766 or British Pat. No. 963,380, with neutralization effected according to procedures disclosed in Canadian Pat. Nos. 674,595 and 713,631, wherein the ionomer is produced by copolymerizing the olefin and carboxylic acid to produce a copolymer having the acid units randomly distributed along the polymer chain. The ionic copolymer comprises one or more alpha-olefins and from about 9 to about 15 weight percent of alpha, beta-ethylenically unsaturated mono- or dicarboxylic acid, the basic copolymer neutralized with metal ions to the extent desired.

At least about 18 percent of the carboxylic acid groups of the copolymer are neutralized by the metal ions, such as sodium, potassium, zinc, calcium, magnesium, and the like, and exist in the ionic state.

Suitable olefins for use in preparing the ionomeric resins include, but are not limited to, ethylene, propylene, butene-1, hexene-1 and the like. Unsaturated carboxylic acids include, but are not limited to acrylic, methacrylic, ethacrylic, alpha-chloroacrylic, crotonic, maleic, fumaric, itaconic acids and the like. Preferably, the ionomeric resin is a copolymer of ethylene with acrylic and/or methacrylic acid.

The covered golf ball can be formed in any one of the several methods known to the art. For example, the molded core may be placed in the center of a golf ball mold and the ionomeric resin-containing cover composition injected into and retained in the space for a period of time at a mold temperature of from about 40° F. to about 120° F.

Alternatively, the cover composition may be injection molded at about 300° F. to about 450° F. into smooth-surfaced hemispherical shells, a core and two

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such shells placed in a dimpled golf ball mold and unified at temperatures on the order of from about 100°F. to about 200° F.

The golf ball produced is then painted and marked, painting being effected by spraying techniques.

The invention is further described in the following examples wherein the parts are by weight unless otherwise specified.

EXAMPLES

Using the ingredients tabled below, golf ball cores having a finished diameter of 1.545 inches were produced by compression molding and subsequent removal of a surface layer by grinding. Each core was formulated using 100 parts high cis content polybutadiene. In the examples, the amounts of remaining ingredients are expressed in parts by weight, and the degrees of coefficient of restitution and compression achieved set forth. The data for each example represents the average data for twelve cores produced in the desired manner.

| Ingredients | EXAMPLES | | | | |
|-----------------------------------|----------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 |
| Zinc Diacrylate | 33.5 | 33.5 | 33.5 | 33.5 | 33.5 |
| Zinc Oxide | 5.5 | 5.5 | 5.0 | 5.0 | 5.0 |
| Stearic Acid | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Ground Flash | 32 | 32 | 16 | 16 | 16 |
| 4,4'-diphenylmethane diisocyanate | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| n-Butyl 4,4-Bis-(Butylperoxide) | 1.5 | 1.5 | 2.0 | 2.0 | 2.0 |
| Valerate | — | 0.4 | — | — | 0.11 |
| Methyl Zimate | — | — | — | 0.6 | 0.6 |
| Dodecanethiol | — | — | — | — | — |
| Weight gms. | 39.2 | 39.3 | 39.6 | 40.1 | 39.4 |
| Compression Riehle | .055" | .056" | .046" | .040" | .052" |
| Coefficient of Restitution | .802 | .803 | .808 | .811 | .807 |

| Ingredients | EXAMPLES | | | |
|---------------------------------|----------|-------|-------|-------|
| | 6 | 7 | 8 | 9 |
| Taktene | 80 | 80 | 80 | 80 |
| BR-11 | 20 | 20 | 20 | 20 |
| Zinc Diacrylate | 31 | 31 | 31 | 31 |
| Ground Flash | 18 | 18 | 18 | 18 |
| Zinc Oxide | 17 | 17 | 17 | 17 |
| Zinc Stearate | 20 | 20 | 20 | 20 |
| n-Butyl 4,4-Bis-(Butylperoxide) | 0.75 | 0.75 | 0.75 | 0.75 |
| Valerate | — | 0.1 | 0.5 | 1.0 |
| Methyl Zimate | — | — | — | — |
| Weight gms | 39.9 | 39.5 | 39.8 | 39.8 |
| Compression Riehle | .062" | .074" | .084 | .084 |
| Coefficient of Restitution | .805 | .805 | .788 | .776 |
| Size | 1.545 | 1.545 | 1.545 | 1.545 |

DISCUSSION OF THE EXAMPLES

The balls of examples 1, 3, 4 and 6 are controls in that they do not incorporate a metallic dithiocarbamate in accordance with this invention. In these examples the compressions are 0.055, 0.046, 0.040 and 0.062 inches respectively for an average of 0.0508, while the coefficients of restitution are 0.802, 0.808, 0.811 and 0.805 respectively for an average of 0.8065. This data indicates that the balls of these examples have satisfactory coefficients of restitution, but that some better golfers may consider them to be hard. Generally, the harder the golf ball, the more difficult it is for a golfer to impart spin to the ball, and, hence, control the ball during play.

The golf balls of examples 2, 5, 7, 8 and 9 incorporate a metallic dithiocarbamate in accordance with this in-

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vention. As can be seen from the data of examples 2, 5, 7 and 8 when a metallic dithiocarbamate is used in accordance with this invention, balls having a very satisfactory coefficient of restitution are produced and yet the balls have significantly higher compressions, indicating that the balls would have a softer feel and, hence, are more readily deformed when struck by a golf club. This additional deformation allows a golfer to put more spin on a golf ball and, hence, impart better control to said golf ball.

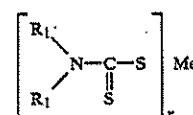
As can be seen, the average coefficient of restitution for these golf balls is 0.8008 and the average compression is 0.0665. This data is to be compared with the control examples 1, 3, 4 and 6 where it can be seen that the average coefficient of restitution for these examples is 0.8065, and the average compression is 0.0508. This decrease of approximately 16 points in the compression as compared to the balls of this invention is very significant as a 16 point decrease would make the resultant golf balls much harder and, hence, more difficult to play. Example 9 demonstrates that when the metallic carbamate is in excessive amounts, the advantages of this invention are mitigated.

As can be seen, golf balls produced in accordance with the present invention maintain satisfactory coefficients of restitution at higher Riehle compressions, such that the resulting golf balls are softer and, hence, more playable.

It will be appreciated that the specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. An improved core composition for a golf ball exhibiting a high coefficient of restitution, said composition comprising an elastomer selected from polybutadiene and mixtures of polybutadiene with other elastomers, at least one metallic salt of an alpha,beta-ethylenically unsaturated monocarboxylic acid, a free radical initiator and a metallic dithiocarbamate having the formula:



wherein R₁ is lower alkyl having from 1 to 5 carbon atoms, Me is a cation having a valence of from 2 to 4 and x is an integer having a value equal to the valence of said cation, said dithiocarbamate present in said composition in an amount of from about 0.1 to about 0.5 parts by weight, based on 100 parts of said elastomer.

2. The composition as defined by claim 1 wherein said elastomer is cis-polybutadiene.

3. The composition as defined by claim 1 wherein said metallic salt is selected from the group consisting of metallic salts of acrylic, methacrylic, itaconic, crotonic and sorbic acids, and mixtures thereof.

4. The composition as defined by claim 3 wherein said metallic salt is zinc diacrylate.

5. The composition as defined by claim 1 wherein said free radical initiator is selected from the group consisting of peroxides, persulfates, hydrazines and azo compounds.

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6. The composition as defined by claim 5 wherein said peroxide is selected from the group consisting of n-butyl-4,4-bis (butylperoxy) valerate, dicumyl peroxide, 1,1-bis (t-butylperoxy) 3,3,5-trimethylcyclohexane, di-t-butyl peroxide and 2,5-di (t-butylperoxy) 2,5-dimethylhexane.

7. The composition as defined in claim 1 wherein said dithiocarbamate is selected from the group consisting of zinc dimethyl dithiocarbamate, zinc diethyl dithiocarbamate, zinc di-n-butyl dithiocarbamate, zinc diamyl dithiocarbamate, tellurium diethyl dithiocarbamate, selenium dimethyl dithiocarbamate, selenium diethyl dithiocarbamate, lead diamyl dithiocarbamate, bismuth dimethyl dithiocarbamate, cadmium diethyl dithiocarbamate, and mixtures thereof.

8. The composition as defined by claim 7 wherein said dithiocarbamate is zinc dimethyl dithiocarbamate.

9. The composition as defined by claim 1 further comprising a modifying ingredient selected from fillers, metal oxides, low molecular weight fatty acids, diisocyanates and mixtures thereof.

10. The composition as defined by claim 9 wherein said ingredient is stearic acid.

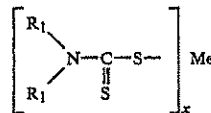
11. The composition as defined by claim 9 wherein said ingredient is 4,4-diphenylmethane diisocyanate.

12. The composition as defined by claim 9 wherein said ingredient is zinc oxide.

13. A golf ball comprising a molded, spherical core and a cover therefor,

said core comprising an elastomer selected from polybutadiene and mixtures of polybutadiene with other elastomers, said elastomer crosslinked with at least one metallic salt of an alpha,beta-ethylenically unsaturated monocarboxylic acid and from about 0.1 to about 0.5 parts by weight, based on 100 parts of said elastomer, of a metallic dithiocarbamate of the formula:

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wherein R₁ is lower alkyl having from 1 to 5 carbon atoms, Me is a cation having a valence of from 2 to 4 and x is an integer having a value equal to the valence of said cation.

14. The golf ball as defined by claim 13 wherein said cover comprises an ionic copolymer of ethylene and an alpha, beta-ethylenically unsaturated monocarboxylic acid selected from the group consisting of acrylic and methacrylic acid wherein from about 20 to about 90 percent of the carboxylic acid groups are neutralized by a metal ion.

15. The golf ball as defined by claim 13 wherein said monocarboxylic acid is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid and mixtures thereof.

16. The golf ball as defined by claim 13 wherein crosslinking of said elastomer is effected by a free radical initiator.

17. The golf ball as defined by claim 16 wherein said initiator is a peroxide.

18. The golf ball as defined by claim 17 wherein said peroxide is selected from the group consisting of n-butyl-4,4-bis (butylperoxy) valerate, dicumyl peroxide, 1,1-bis (t-butylperoxy)-3,3,5-trimethylcyclohexane, di-t-butyl peroxide and 2,5-di (t-butylperoxy)-2,5-dimethylhexane.

19. The golf ball as defined by claim 13 wherein Me is selected from the group consisting of zinc, tellurium, selenium, lead, copper, bismuth and cadmium.

20. The golf ball as defined by claim 19 wherein said dithiocarbamate is zinc dithiocarbamate.

21. The golf ball as defined by claim 13 wherein said core further comprises a modifying ingredient selected from fillers, metal oxides, low molecular weight fatty acids, diisocyanates and mixtures thereof.

22. The golf ball as defined by claim 21 wherein said fatty acid is stearic acid.

23. The golf ball as defined by claim 21 wherein said diisocyanate is 4,4-diphenylmethane diisocyanate.

24. The golf ball as defined by claim 21 wherein said metal oxide is zinc oxide.

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EXHIBIT 11

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

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EXHIBIT 12

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1 UNCERTIFIED REALTIME ROUGH DRAFT

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3 You have requested an unedited, uncertified
4 transcript. This rough draft transcript has been
5 requested in the form of either a realtime hookup to
6 your computer or an ASCII file delivered after the
7 close of proceedings.

8 This realtime transcript is available only to
9 counsel who order a certified original or a certified
10 copy of today's proceedings.

11 This realtime draft is unedited and uncertified and
12 may contain untranslated stenographic symbols,
13 misspelled proper names and/or nonsensical word
14 combinations. All such entries will be corrected on
15 the final certified transcript and final ASCII file.

16 Due to the need to correct entries prior to
17 certification, it is agreed this realtime draft will
18 be used only to augment counsel's notes and will not
19 be cited in any court proceedings or distributed to
20 any other parties.

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ROUGH DRAFT TRANSCRIPT

1 THE VIDEOGRAPHER: This is tape No. 1 of the
2 videotaped deposition of Edward M. Caulfield taken by
3 the Plaintiff/Counterclaim Defendant in the matter of
4 Bridgestone Sports Company, Limited, et al., versus
5 Acushnet Company and the appropriate counterclaim
6 pending in the US District Court for the District of
7 Delaware, Case No. 05-132 (JJF).

8 This deposition is being held at 3003
9 Corporate West Drive in Lisle, Illinois on March 29,
10 2007. The time on the video screen is 9:04 AM.

11 My name is Ben Stanson. I'm the
12 legal videographer from Digital Evidence Group. The
13 Court Reporter today is Shannon Frey, also in
14 association with Digital Evidence Group.

15 Will Counsel please introduce
16 themselves for the record.

17 MS. STASIO: Renee Stasio with Howrey for
18 Acushnet Company.

19 MR. JENKINS: Tom Jenkins from Howrey for
20 Acushnet Company.

21 MR. WIKBERG: Terry Wikberg from Paul Hastings
22 for Bridgestone Golf Company and Bridgestone Sports,
23 and with me is Kevin Jones from Packer Engineering.

24 THE VIDEOGRAPHER: Thank you. Will the court

1 specific point that they have, but the bounce tests
2 for rebound having run on an enormous amount of
3 materials.

4 The bowling ball industry does that
5 over and over again for restitution and resilience of
6 their balls and pins.

7 So I guess what I'm saying is those
8 material properties aren't news to me.

9 Q. Okay. Are there any instances when you
10 ever stray from the standard way you would measure a
11 material property in polymer science?

12 MR. WIKBERG: Objection; vague.

13 BY THE WITNESS:

14 A. I would say at times during testing if you
15 can't do it exactly as maybe supplied by a standard,
16 you can deviate from the methodology with engineering
17 discretion.

18 BY MS. STASIO:

19 Q. What does engineering discretion mean?

20 A. You know if the standard says did it this
21 way, and, for example, if it says measure the density
22 in water and you can't measure it in water so you
23 measure it in isopropyl alcohol instead. That's
24 another way of measuring the density.